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Industrial Process Profiles for Environmental Use: Chapter 30. The Electronic Component Manufacturing Industry

PEDCo-Environmental, Inc.
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INDUSTRIAL PROCESS PROFILES FOR ENVIRONMENTAL USE:
CHAPTER 30
THE ELECTRONIC COMPONENT MANUFACTURING INDUSTRY

by

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Contract No. 68-03-2924

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16. ABSTRACT

This report is one of a series constituting the catalog of Industrial Process Profiles for Environmental Use. Each industry sector is addressed as a separate chapter of the study. The catalog was developed for the purpose of compiling relevant information concerning air, water, and solid waste emissions from industries which employ similar technologies, have common types of environmental impacts, and supply their products for further processing or consumption to the same general population of customers. Each industrial process is examined from the standpoint of its function, feed materials, operating conditions, utility requirements, and waste streams. A completed IPPEU report constitutes a multimedia data base of the environmental impacts of an industry's production operations based upon information available in the open literature. As such, it is preliminary in nature and should be viewed as the first step in development of a comprehensive analysis of environmental impacts. This report addresses the following segments of the electronic component manufacturing industry: semiconductors, SIC 3674; capacitors, SIC 3675; resistors, SIC 3676; transformer and inductors, SIC 3677; printed circuit boards, SIC 3679052; electron tubes, SIC 36711, 36713; and cathode ray tubes, SIC 36712, 3671385.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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CONTENTS

Page

Figures vi
Tables viii

1. Introduction 1

2. Semiconductors 7

    Industry description 7
    Industry analysis 24
      Process No. 1, wafer cutting, smoothing, and polishing 27
      Process No. 2, chemical cleaning and polishing 30
      Process No. 3, epitaxial growth 32
      Process No. 4, circuit fabrication 37
      Process No. 5, diffusion 41
      Process No. 6, metal interconnection 44

3. Capacitors 50

    Industry description 50
    Industry analysis 61
      Tantalum wet and dry slug capacitors
        Process No. 1, anode fabrication 68
        Process No. 2, formation reactions 69
        Process No. 3, forming 70
        Process No. 4, acid/carbon slurry dips 71
        Process No. 5, assembly (dry slug) 72
        Process No. 6, assembly (wet slug) 73
      Tantalum foil capacitors
        Process No. 1, electrochemical oxide formation 74
        Process No. 2, assembly 75
      Glass encapsulated capacitors
        Process No. 1, assembly 76
        Process No. 2, terminal cleaning 77
        Process No. 3, glass cutting 78
      Aluminum electrolytic capacitors
        Process No. 1, oxide formation 79
        Process No. 2, assembly 80

CONTENTS (continued)

Page

Mica capacitors

Process No. 1, dielectric fabrication 81

Ceramic capacitors

Process No. 1, ball milling 82
Process No. 2, ceramic formation 83
Process No. 3, baking/printing 84
Process No. 4, assembly 87

4. Resistors 89

Industry description 89
Industry analysis 100
Process No. 1, resistive element formation 102
Process No. 2, impregnation and coating application 106
Process No. 3, assembly and lead attachment 108
Process No. 4, protective cover formation 110

5. Transformers and Inductors 114

Industry description 114
Industry analysis 120
Process No. 1, core fabrication 125
Process No. 2, coil winding 130
Process No. 3, impregnation and coating 132
Process No. 4, encapsulation 135

6. Printed Circuit Boards 137

Industry description 137
Industry analysis 143
Process No. 1, board preparation 147
Process No. 2, board cleaning 149
Process No. 3, surface preparation 151
Process No. 4, catalyst application 153
Process No. 5, electroless plating (flash) 154
Process No. 6, image transfer 158
Process No. 7, electroplating 162
Process No. 8, etching 170
Process No. 9, multilayer board lamination 175

7. Electron Tubes 178

Industry description 178
Industry analysis 183
Process No. 1, tube mount assembly 187
Process No. 2, glass mount assembly 189
Process No. 3, gettering/final assembly 190

CONTENTS (continued)

Page

8. Cathode Ray Tubes 192

Industry description 192
Industry analysis 196
Process No. 1, aperture mask manufacturing 198
Process No. 2, aperture mask degreasing 200
Process No. 3, glass panel wash 202
Process No. 4, photoresist application 203
Process No. 5, phosphor application 205
Process No. 6, glass funnel preparation 208
Process No. 7, shield degreasing 209
Process No. 8, electron gun assembly 210
Process No. 9, final tube assembly 211
Process No. 10, picture tube reclaim 212

Appendix Wastewater treatment and control 214

FIGURES

Number		Page
1-1	Value of Total Shipments (Primary, Secondary, and Miscellaneous) - Electron Tube and Semiconductor Industries	3
2-1	FET Bar Structure	9
2-2	N-channel Enhancement-Mode MOSFET Formation	9
2-3	World Total Semiconductor Production	14
2-4	Worldwide Shipments by U.S. Companies of Discrete Semiconductors	15
2-5	World Discrete Semiconductor Market for Worldwide Suppliers	16
2-6	Transistor and Diode Production Flowsheet	25
2-7	Integrated Circuit (IC) and Light Emiting Diode (LED) Production Flowsheet	26
3-1	Capacitor Sales: A Comparison of Growth Over the Past Decade	56
3-2	Tantalum Wet and Dry Slug Capacitor Production Flowsheet	62
3-3	Tantalum Foil Capacitor Production Flowsheet	63
3-4	Glass Encapsulated Capacitor Production Flowsheet	64
3-5	Aluminum Electrolytic Capacitor Production Flowsheet	65
3-6	Ceramic Capacitor Production Flowsheet	66
4-1	Sales of Major Resistor Types, 1977-1979	92
4-2	Resistor Production Flowsheet	101
5-1	Transformer Production Flowsheet	124

FIGURES (continued)

Number		Page
6-1	Additive Printed Circuit Board Production Flowsheet	144
6-2	Subtractive Printed Circuit Board Production Flowsheet	145
6-3	Semi-additive Printed Circuit Board Production Flowsheet	146
7-1	Receiving-type Electron Tube Production Flowsheet	184
7-2	Transmitting Electron Tube Production Flowsheet	185
8-1	Color Television Picture Tube Production Flowsheet	197
8-2	In-place Waste Treatment for Hexavalent Chromium Wastes from a Picture Tube Manufacturing Process	204
8-3	In-Place Waste Treatment for Phosphor Wastes from a Picture Tube Manufacturing Process	207
A-1	Wastewater Treatment System - Semiconductor Manufacture	215
A-2	Wastewater Treatment System - Printed Circuit Board Manufacture (Segregated Waste Streams).	220

TABLES

Number		Page
1-1	Electronic Components Industry - 1977 Statistics	2
2-1	U.S. Sales of Semiconductor Devices	13
2-2	Company Size Distribution by Total Employment for Semiconductors and Related Devices	17
2-3	World Discrete Market Share Estimates	19
2-4	Some Manufacturers of Discrete Semiconductors	20
2-5	Number of Companies Producing Various Semiconductors and the Quantity of Shipments of Each Type	21
2-6	Characteristics of Raw Waste Streams from Semiconductor Device Manufacturing	23
2-7	Semiconductor Machining Waste for a Typical Plant	29
2-8	Indirect Epitaxial Growth Techniques	34
2-9	Semiconductor Process Waste for an Isolated Plant	36
2-10	Semiconductor Process Wastes for the Circuit Fabrication Process	40
2-11	Common Diffusion Sources for Open Tube Systems	42
2-12	Metal Interconnection Etch Rinse for an Isolated Plant	47
3-1	Capacitor Sales Over Past 10 Years	55
3-2	Forecast for Capacitor Sales	57
3-3	Number of Companies Manufacturing Various Capacitor Types	58
3-4	Size Breakdown of Capacitor Producers Based on Total Employment	59
3-5	Major Monolithic Ceramic Manufacturers	60

TABLES (continued)

Number		Page
3-6	Analysis of Process Wastewater from a Ceramic Capacitor Ink Manufacturing Operation	85
4-1	Industry-wide Consumption of Resistors Shipped by U.S. and Foreign Manufacturers for the U.S. Market	93
4-2	Number of Companies Producing Each Resistor Type	95
4-3	Resistor Manufacturers by Employment Range Classification	96
4-4	Major Manufacturers of Fixed Resistors	97
4-5	Major Manufacturers of Variable Resistors	98
4-6	Market Shares of Major Resistor Suppliers	99
4-7	Characteristics of Alloys Used in Wire-wound Potentiometers and Resistors	104
5-1	High Permeability Materials and Alloys	117
5-2	Shipments of Electronic Transformers, Inductors, and Coils	118
5-3	Market Estimates for Coils, Transformers, and Chokes	119
5-4	Companies Manufacturing Various Products Under SIC 3677	121
5-5	Distribution of Company Size in SIC 3677 by Total Employment	122
5-6	Transformer and Inductor Manufacturers	123
5-7	High-Permeability Nickel-Iron Alloys	127
5-8	Cobalt-Iron Alloys	128
6-1	Printed Circuit Board Sales	140
6-2	Characteristics of Raw Waste Streams from Printed Circuit Board Manufacturing	142
6-3	Typical Electroless Copper Plating Baths	156
6-4	Additives Used in Photosensitive Resists	161
6-5	Plating Bath Constituents	163

TABLES (continued)

Number		Page
6-6	Common Operating Conditions for Plating Baths	166
6-7	Diatomaceous Earth Filtration Performance Data	168
6-8	Ion Exchange Performance Data	168
6-9	Characteristics of $FeCl_3$ Solutions	171
6-10	Composition of Typical Persulfate Etch Solutions	171
6-11	Composition of Typical Chromic-Sulfuric Acid Etch Solutions	172
6-12	Composition of Typical Cupric Chloride Etch Solutions	172
6-13	Composition of Typical Alkaline Etch Solutions	173
7-1	Receiving-Type Electron Tube Manufacturers and Product Shipments	181
7-2	Transmitting and Special-Purpose Electron Tube Product Shipments	182
8-1	Companies Producing CRT's for Televisions	195
8-2	Summary of Raw Waste Data from an Aperture Mask Manufacturing Operation	199
8-3	Summary of Raw Waste for Television Picture Tube Manufacture	201
A-1	Performance of Chemical Precipitation and Sedimentation - Semiconductor Manufacture	217
A-2	Performance of Fluoride Treatment Systems - Semiconductor Manufacture	218

SECTION 1

INTRODUCTION

In recent decades electronic equipment has become an integral part of modern technological society. Computers, sophisticated communications systems and industrial and military hardware, entertainment equipment, and other electronic devices are in widespread usage. This equipment is manufactured from many individual electronic components, which in turn may be made from any of thousands of different substances. This report to the U.S. Environmental Protection Agency (EPA) is a preliminary assessment of the potential environmental impacts associated with the production of these components in the United States.

The electronic components industry is large and complex, and many segments are experiencing rapid changes in technology. Hundreds of individual component types are manufactured. Table 1-1 presents statistical data on the industry.[1] Total sales of primary products in 1977 were over $14 billion, and overall the industry has been growing at a fast pace. The largest single segment of the industry, with $4.5 billion in sales, is semiconductors and related devices. This is also a rapidly growing category; the value of shipments increased 92 percent between 1972 and 1977. However, some segments of the industry face a much different outlook. Older product types are being replaced in many applications by newer solid-state technologies. This is illustrated in Figure 1-1, which shows comparative data on the value of total shipments for the semiconductor and electron tube industries from 1963 to 1977.[1]

Although there are changes taking place in the types and quantities of specific components being manufactured, there should continue to be strong growth for the industry in the future. This will be especially true of microelectronic components, already one of the most rapidly growing industries in the United States. Although the microprocessor was invented only ten years

TABLE 1-1. ELECTRONIC COMPONENTS INDUSTRY - 1977 STATISTICS[1]

Product	Number of establishments	Employment			Primary shipments	
		Number of employees	1972-1977 increase, %	Leading states	$ million	1972-1977 increase, %
Electron tubes, all types	146	36,700	12	NY, PA, CA	1,257	6
Semiconductors and related devices	545	114,000	17	NY, TX, AZ, CA	4,532	92
Capacitors	118	28,900	5	PA, NC, SC, CA	736	62
Resistors	101	21,300	4	PA, IN, CA	583	33
Coils and transformers	294	20,700	-13	NY, IL, CA	606	57
Connectors	133	26,000	44	NY, PA, IL, CA	986	88
Others[a]	3,119	126,000	25	MA, NY, IL, CA	5,574	74
Total	4,456	373,600	11		14,274	67

[a] Printed circuit boards, modular components, magnetic recording media, antennas, microwave devices, filters, crystals, etc.

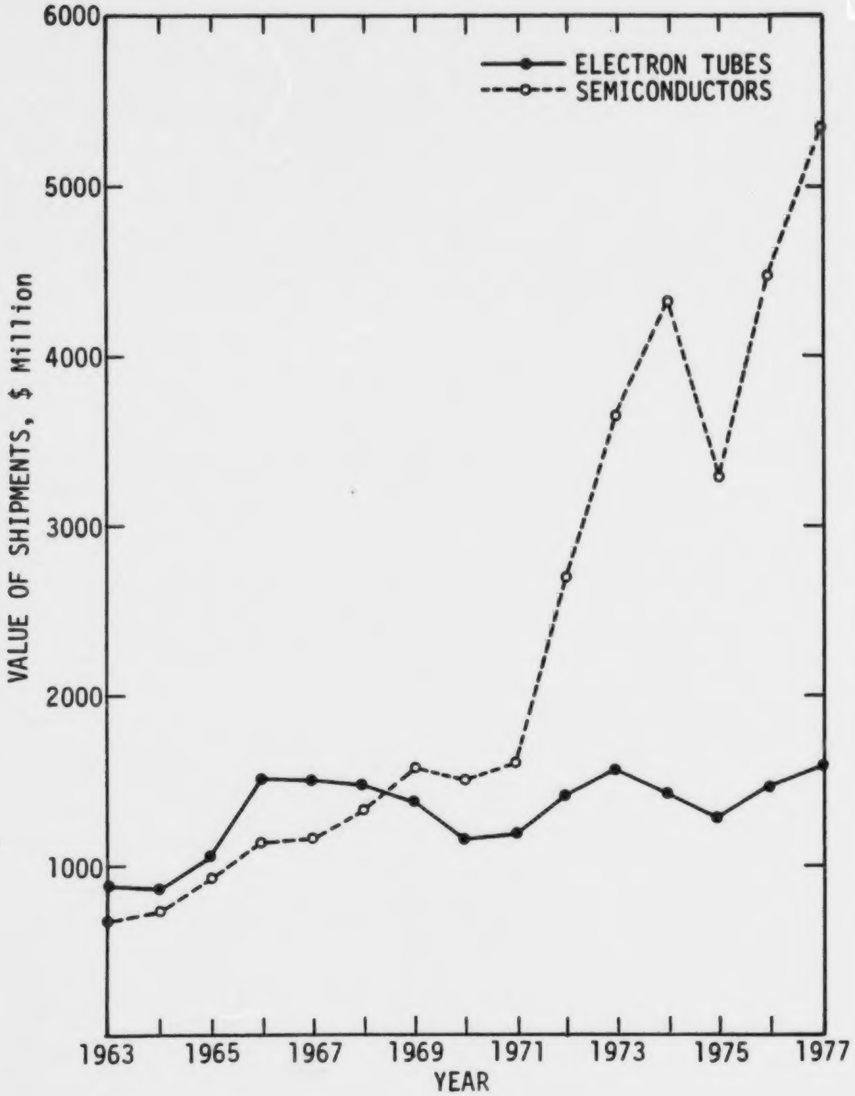

Figure 1-1. Value of total shipments (primary, secondary, and miscellaneous) - electron tube and semiconductor industries.[1]

ago, these chips are now used in an incredible variety of manufactured goods. Microelectronic devices that were no more than an expensive curiosity a few years ago are now commonplace. There will be increasing use of these components for applications in our homes, industries, schools, and transportation equipment in the future.

The potentially hazardous and toxic nature of some substances used to make electronic components, coupled with the continued growth forecast for the industry, suggests that such emissions from these emitting production processes be controlled to achieve continuous compliance with established standards. In 1977 there were nearly 4,500 manufacturing establishments spread throughout the country, an increase of 50 percent over a five-year period.[1,2] In addition, nearly 400,000 persons were directly employed in these facilities in 1977; this represents 1.9 percent of the total U.S. manufacturing work force.[1,3]

As indicated, there are hundreds of individual electronic components. Many are manufactured with similar processes. For the purposes of this analysis, EPA has requested that the following segments be analyzed:

		SIC Code
1.	Semiconductors	3674
2.	Capacitors	3675
3.	Resistors	3676
4.	Transformers and inductors	3677
5.	Printed circuit boards	3679052
6.	Electron tubes	36711, 36713
7.	Cathode ray tubes	36712, 3671385

The analyses in this report are in the format of the Industrial Process Profiles for Environmental Use (IPPEU).[4] This format was developed by EPA's Industrial Environmental Research Laboratory for the purpose of cataloging relevant information concerning air, water, and solid waste emissions from industries which employ similar technologies, have common types of environmental impacts, and supply their products for further processing or consumption to the same general population of customers. Each industrial process is examined from the standpoint of its function, feed materials, operating conditions, utility requirements, and waste streams. A completed IPPEU report constitutes a multimedia data base on the environmental impacts of an industry's production operations based upon information available in the open literature. As such, it is preliminary in nature and should be viewed as the first step in development of a comprehensive analysis of environmental impacts. Major pollution problems are identified, and any gaps in the data base are readily apparent. The final report thus serves to direct fact-finding research and development needed to reduce environmental problems. It should also provide sufficient data to allow a focus on problems that have the most adverse effect on public health and welfare.

Rapid technological changes are taking place in the industry, and many operations are proprietary in nature. Because the IPPEU report is based only upon information found in the open literature, few details were found of many aspects of some production processes. This preliminary report summarizes the available data. It was prepared by PEDCo Environmental, Inc., of Cincinnati, Ohio; PEDCo was assisted in this effort by Centec Consultants of Reston, Virginia. Mr. John O. Burckle was Project Officer for EPA's Industrial Environmental Research Laboratory in Cincinnati.

Sections 2 through 8 present the IPPEU analyses of the individual segments of the electronic components industry. Each section is divided into two parts: an Industry Description, which presents an overview of the raw materials, products, and companies associated with each component type; and an Industry Analysis, which presents specific information on production processes and discharges. An appendix presents additional information on wastewater control and treatment in the industry.

REFERENCES FOR SECTION 1

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2. U.S. Department of Commerce. 1972 Census of Manufactures: Electrical Components and Accessories.
3. U.S. Department of Commerce. 1977 County Business Patterns: U.S. Summary.
4. U.S. Environmental Protection Agency. Industrial Process Profiles for Environmental Use. Chapter 1: Introduction. PB-266274. January 1977.

SECTION 2

SEMICONDUCTORS

INDUSTRY DESCRIPTION

A semiconductor material is one whose electrical conductivity falls between that of a conductor and that of an insulator. In the electronic components industry, the term semiconductor covers a wide range of devices whose main functioning parts are composed of a semiconductor material; these include transistors, diodes, thyristors, and integrated circuits. These solid state devices have no moving parts and are used for information processing, display purposes, power handling, and conversion of light to energy.

Semiconductor components now manufactured are many times smaller than the equivalents of even a few years ago. They meet today's needs for high component density in many electronic applications. Generally, semiconductor devices are mounted on printed circuit boards as part of a larger circuit. Discrete devices are used for relatively simple circuitry, where processing needs do not place unusual demands on semiconductor electrical characteristics. Many semiconductor components can be integrated into a single processor chip to meet greater density demands. The following paragraphs present an overview of the major types of semiconductor components.

Transistors consist of a small block of semiconductor material with three or more electrodes. Similar to electron tubes in use (i.e., amplification and rectification), transistors are constructed of various semiconductor materials and additional impurities ("dopants") such as boron, aluminum, gallium, or indium. The semiconductor materials are referred to as "P-type" or "N-type" depending on their ability to accept or donate electrons to the atomic structure. There are three broad categories of transistors: bipolar, field effect, and unijunction.

Bipolar (or multijunction) transistors have a base and two junctions (emitter, collector) with terminals attached to each. Junctions of bipolar transistors are formed by either alloying donor or acceptor material to a thin, doped semiconductor pellet; by diffusion of dopants into a doped silicon or germanium wafer; by formation of the junctions during crystal growth; or by a combination of crystal growth and diffusion.[1]

Field-effect transistors (FET) are also three-layered devices but are voltage-actuated rather than current-actuated. Conduction is by the flow of majority carriers through a conduction channel controlled by voltage applied between the gate and source terminals. One type of FET is the junction field-effect transistor (JFET), which consists of a bar of doped silicon with semiconductor materials diffused into it. A typical JFET structure is shown in Figure 2-1. Another type of FET, the metal-oxide-semiconductor field effect transistor (MOSFET), differs in both structure and control mechanism. Two separate low-resistivity regions (source and drain) are diffused into a high-resistivity substrate. The surface is then covered with an oxide layer to insulate the channels from the gate and a silicon nitride layer to protect the oxide layer from sodium ion contamination. This type of MOSFET is shown in Figure 2-2. MOSFET applications include RF amplifiers, mixers, oscillators, audio and wide band amplifiers, variable attenuators, choppers, and current limiters.[1]

Unijunction transistors (UJT) have one junction and a stable negative resistance characteristic between the emitter and base 1 terminals when a positive bias voltage is applied between base 1 and base 2 terminals.

Diodes are semiconductor devices with two terminals that find uses analogous to electron tube diodes. They include semiconductor rectifier diodes, zener diodes, varactors (voltage variable capacitors), tuning diodes, and silicon diode capacitors. Semiconductor rectifier diodes may be made from germanium, selenium, copper oxide, and, most commonly, silicon. One type called a point-contact diode consists of a sharp-pointed fine wire attached to a semiconductor crystal. These have superior high-frequency characteristics and some types can even operate at microwave frequencies. Junction rectifier diodes operate at a much lower frequency than point-contact diodes, but have higher power dissipation capabilities. Zener (or breakdown) diodes are two-layered devices that exhibit a sharp rise in current flow when an applied

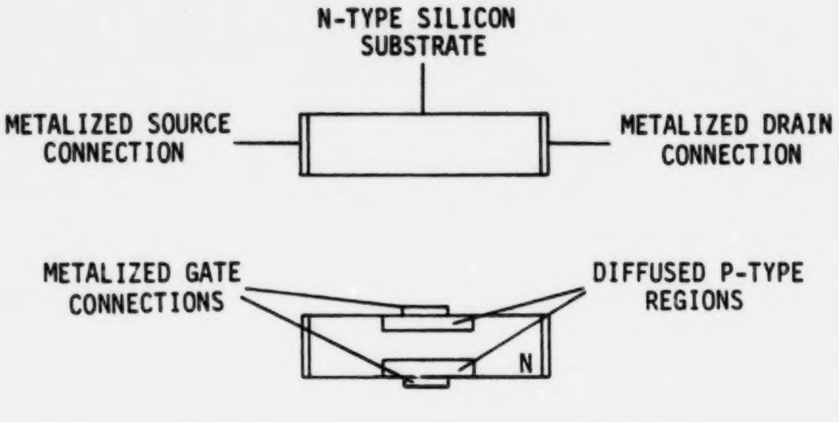

N-TYPE SILICON SUBSTRATE
METALIZED SOURCE CONNECTION
METALIZED DRAIN CONNECTION
METALIZED GATE CONNECTIONS
DIFFUSED P-TYPE REGIONS
N

Figure 2-1. FET bar structure.[1]

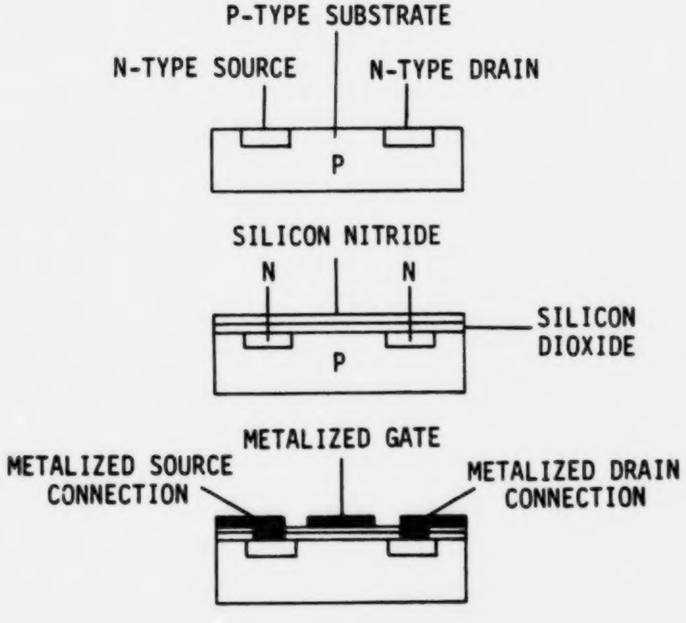

P-TYPE SUBSTRATE
N-TYPE SOURCE
N-TYPE DRAIN
P
SILICON NITRIDE
N
N
SILICON DIOXIDE
P
METALIZED GATE
METALIZED SOURCE CONNECTION
METALIZED DRAIN CONNECTION

Figure 2-2. N-channel enhancement-mode MOSFET formation.[1]

reverse-bias voltage is increased to the region of the breakdown voltage. When forward-bias voltage is applied, the zener diode functions as an ordinary rectifier. They are used for voltage regulation, overvoltage protection, and to provide a reference voltage.[1]

Thyristors (also called silicon controlled rectifiers [SCR's]), silicon controlled switches (SCS's), and triacs are semiconductor switching devices that have three or more junctions. These devices act to rectify a main AC or DC current by normal diode action, but conduct only when an external signal or voltage applied at the gate terminal exceeds a certain amount. It ceases to conduct if that voltage is reduced below threshold or if the gate current is switched off.

Integrated circuits (IC's) are electronic subassemblies consisting of a number of elements placed together on a semiconductor chip. These elements are primarily diodes and transistors yet are often used to perform activities associated with components. They can be used in almost any electronic application that involves small AC or DC signals. IC's can be divided into two broad categories, digital (or switching) circuits and analog (or linear) circuits. Digital circuits are further classified by the system logic; for example, TTL (transistor-transistor logic), DTL (diode-transistor logic), ECL (emitter-coupled logic) and RTL (resistor-transistor logic). MOS (metal-oxide-semiconductor) digital circuits are more sophisticated and are subdivided. Linear IC's can be classified as operational amplifiers, voltage regulators, audio amplifiers, television modules, radio tuners, IF amplifiers, and others.[2]

Raw Materials

Raw materials for the manufacture of semiconductors can be categorized into groups that include semiconductor base materials, dopants, passivating and insulating materials, and metals:[3,4,5]

- Base materials - Silicon is the most widely used base material (substrate) in the semiconductor industry, finding applications in 90 to 96 percent of all products. The silicon must be of extremely high quality; impurities are as low as one part per billion. Germanium is used primarily in the production of discrete devices such as diodes. First used in this regard in the early 1950's, it is still manufactured to supply and maintain existing equipment, but has been replaced by silicon in most recent applications. Gallium arsenide (GaAs) and gallium phosphide (GaP) are used primarily in the production of light emitting diodes (LED's). Use of gallium arsenide in photovoltaics for space and terrestrial applications is also increasing.

- Dopants - Dopants are added to the semiconductor to increase conductivity. The commonly used dopants for silicon are boron, phosphorus, arsenic, and antimony. Phosphine gas (PH_3) or phosphorous oxychloride ($POCl_3$) are usually used for phosphorus diffusion. Boron trichloride (BCl_3) or diborane (B_2H_4) gases are usually used for diffused junction formation with boron. Boron trifluoride (BF_3) may also be used, as well as pure boron powder. Other dopants include arsine gas (AsH_4), arsenic hexafluoride (AsF_6), arsenic, antimony, aluminum, gallium, gold, beryllium, germanium, magnesium, silicon, tin, and tellurium.

- Passivating and insulating materials - The two most commonly used materials are silicon dioxide (SiO_2) and silicon nitride (Si_3N_4). A silicon dioxide layer may be deposited by using silicon dioxide, vaporized silicon and oxygen gas, or by silane (SiH_4) and nitrous oxide (N_2O) gases. Silicon nitride may be deposited by chemical vapor deposition using dichlorosilane (SiH_2Cl_2) and ammonia (NH_3).

- Metals - Metals are sputtered or evaporated onto the surface of the wafer to provide electrical contacts. These metals include aluminum, gold, chromium, tin, palladium, nickel, titanium, copper, and platinum, as well as various combinations. Some metals may be electroplated onto the wafer's metal surface to provide the external contacts. These include gold, tin, copper, silver, and chromium.

- Processing materials - Other major processing materials include acid and alkaline cleaners, resists (etchant resistive materials), flammable solvents, chlorinated solvents, and etch solutions. These include a broad range of formulations (many proprietary).

Products

The semiconductor industry comprises establishments primarily engaged in the manufacture of semiconductors and related solid-state devices such as semiconductor diodes and stacks. This includes rectifiers, integrated microcircuits (semiconductor networks), transistors, solar cells, thyristors, light sensing and emitting semiconductor (solid-state) devices, microprocessors, and solid-state memory devices. The Bureau of the Census classifies semiconductors and related devices into SIC 3674.[6]

Shipments of U.S. primary semiconductor products increased 92 percent from 1972 to 1977.[6] Integrated microcircuits and semiconductor networks accounted for a significant portion of that increase. Total estimated 1980 sales of all semiconductors, including integrated circuits, were $6,360.5 million.[7] A breakdown of products and total sales from one industry source is presented in Table 2-1.[7] Projected sales for 1983 are $11,074 million, which represents an annual increase of 18.9 percent. However, one recent article reported that the discrete semiconductor sales for 1981 are expected to increase by only about 4 percent. The following year (1982) is expected to see a 10 percent increase.[8]

Integrated circuits comprise by far the greatest portion of the market. Estimated 1980 IC sales were about 77 percent of the total semiconductor industry.[7] By 1983 this share is expected to increase to about 82 percent.[7] A comparison of world production of IC's and discrete semiconductors is shown in Figure 2-3.[8] In 1980, power transistors accounted for about 21 percent of the total shipment of discrete semiconductors, making this the biggest product area among discrete components.[8] Optoelectronics (solar cells, photoconductive cells, LED's, photodiodes, phototransistors, couplers, and fiber optics) comprised the second largest category, almost 19 percent of total shipments. Optoelectronics, however, is expected to overtake power transistors as the largest product category among discrete components in the next two to three years.[8] Figure 2-4 presents estimated worldwide shipments by U.S. companies of various categories of discrete semiconductors from 1979 to 1983.[8] A breakdown of estimated world market share by type is shown in Figure 2-5.[8] On a worldwide basis, power transistors should continue to hold the largest share, followed by rectifiers and optoelectronics.

Companies

The Bureau of the Census reports that approximately 545 companies are engaged in the manufacture of semiconductors and related devices in the United States.[6] Table 2-2 shows the size distribution of companies by total employment.[6] However, an August 1979 listing of plant locations compiled by the Semiconductor Industry Association lists only 257 plants involved in the production of semiconductor devices. Table 2-3 shows major world producers of

TABLE 2-1. U.S. SALES OF SEMICONDUCTOR DEVICES, $ million[7],[a]

Product	Year				Annual growth, %
	1978	1979	1980	1983	
Total semiconductors	3,937.6	5,061.7	6,360.5	11,074	18.9
Discrete semiconductors	1,035.6	1,137.1	1,202.2	1,523	7.1
Diodes	370.2	398.2	421.9	548	6.8
Transistors (includes bipolar MOSFET, and junction FET)	533.9	606.6	640.4	788	7.8
Signal transistors	251.0	269.3	283.3	321	5.2
Thyristors	114.5	115.0	122.4	162	9.0
Integrated circuits	2,694.5	3,684.1	4,876.3	9,121	22.3
Standard logic facilities (includes RTL, DTL, TTL, ECL and C-MOS)	813.1	1,011.0	1,192.8	1,784	15.3
Microprocessors and microcomputers (includes CPU's, one-chip microcomputers, LSI peripheral chips)	210.9	330.8	532.4	1,506	31.9
Dedicated LSI circuits	95.5	155.0	210.5	595	31.1
Memories (includes random-access read-only, CCD's, magnetic-bubble devices and shift registers)	850.3	1,289.7	1,922.2	3,560	27.4
Linear IC's	594.7	681.1	746.4	1,158	11.1
Consumer product IC's	130.0	216.5	272.0	518	25.4
Optoelectronic devices (includes photovoltaic cells, photoconductive cells, LED's, laser diodes, photodiodes, phototransistors, and optically coupled isolators	207.5	240.5	282.0	430	13.3

[a] Dollars represent actual volume of sales unadjusted for inflation.

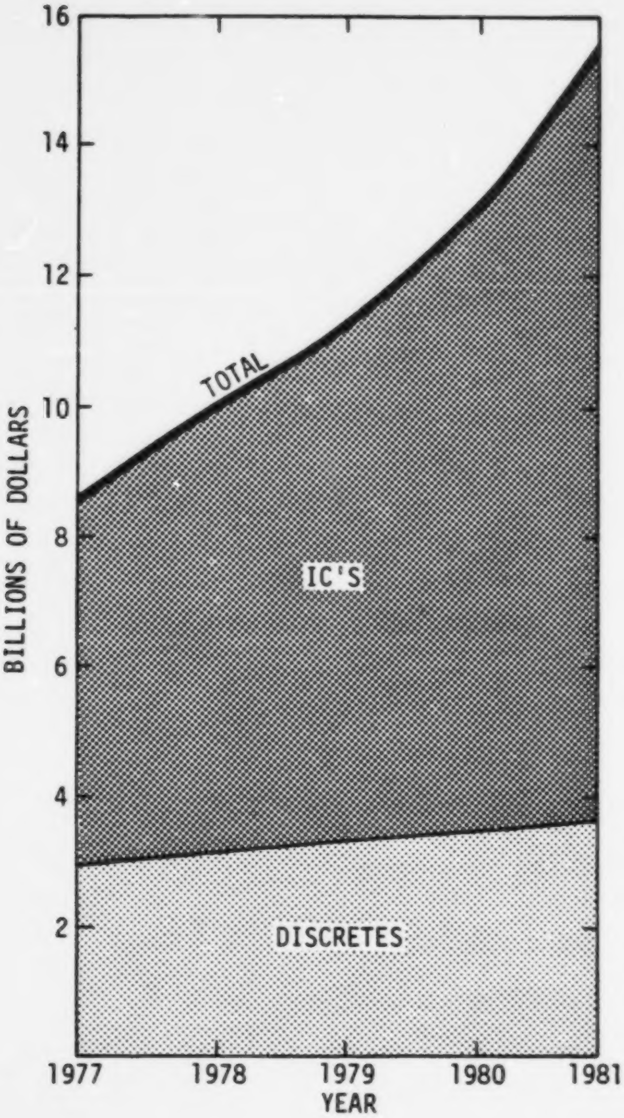


Figure 2-3. World total semiconductor production.[8]

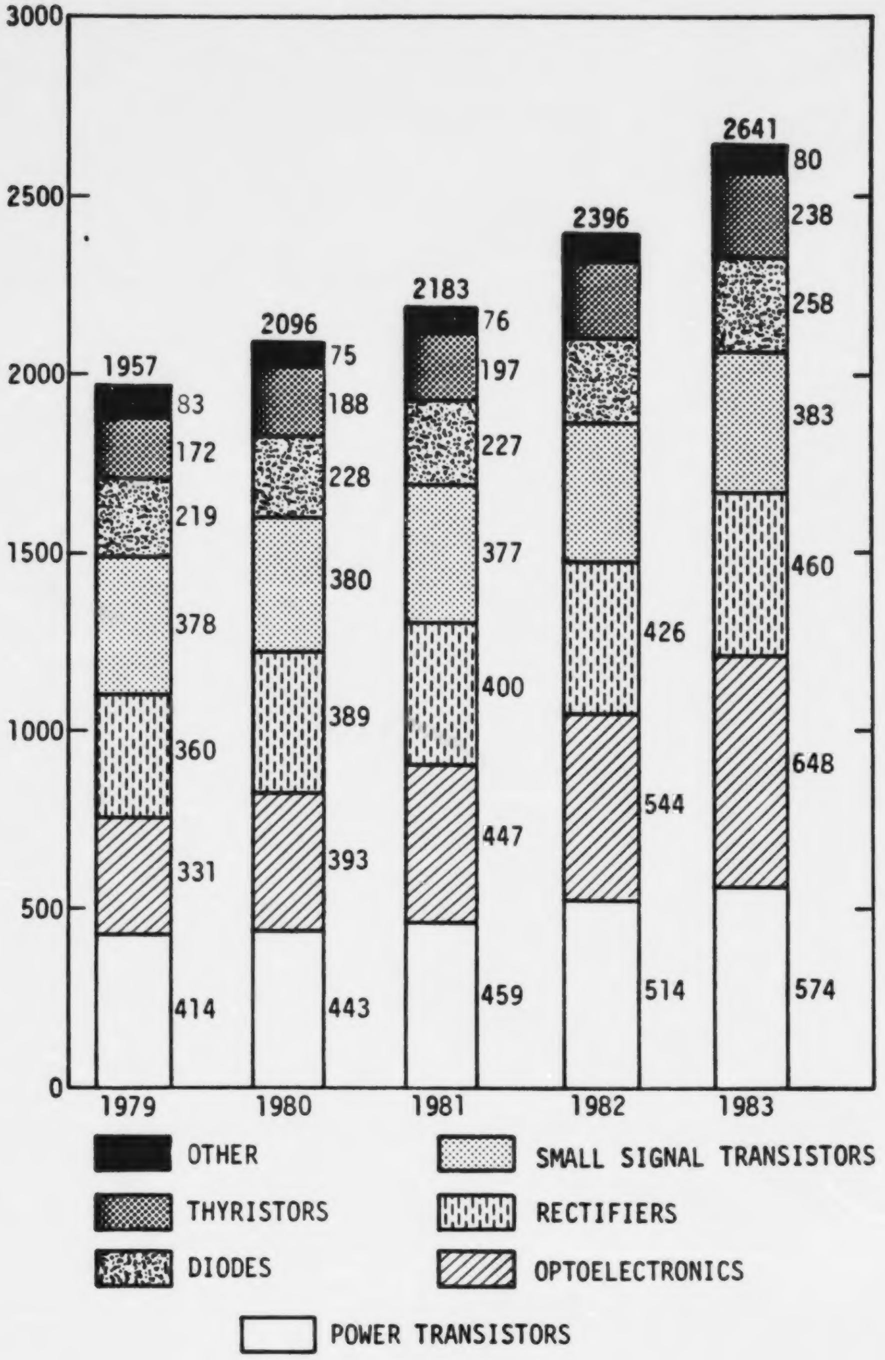


Figure 2-4. Worldwide shipments by U.S. Companies of discrete semiconductors ($ million).[8]

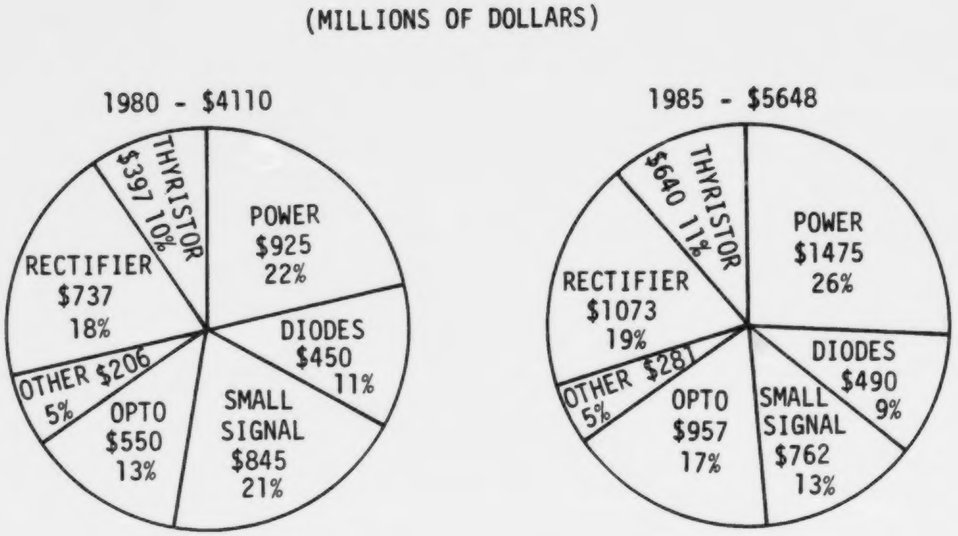


Figure 2-5. World discrete semiconductor market for worldwide suppliers ($/million).[8]

TABLE 2-2. COMPANY SIZE DISTRIBUTION BY TOTAL EMPLOYMENT FOR SEMICONDUCTORS AND RELATED DEVICES[6]

Employment range	Number of companies
1 to 4 employees	191
5 to 9 employees	75
10 to 19 employees	80
20 to 49 employees	48
50 to 99 employees	40
100 to 249 employees	59
250 to 499 employees	31
500 to 999 employees	19
1,000 to 2,499 employees	10
2,400 employees or more	12
TOTAL	545

discrete semiconductor devices and their estimated share of the total market.[8] Table 2-4 gives a small sample of semiconductor manufacturers and their product lines.[8] Finally, Table 2-5 gives a breakdown of the number of companies producing each type of semiconductor.[6]

Environmental Impacts

Air emissions from semiconductor device manufacturing include acid fumes and chlorinated organic solvent vapors. Acid fumes originate from solutions used in most wet processes. Chlorinated organic solvent vapors are primarily the result of surface cleaning and developing and stripping of resists. Control of air emissions involves collection of contaminated air streams using hoods above processing baths and equipment, followed by wet scrubbing. Contaminant removal is based on segregation and treatment of similar air streams.

Total process water flow from semiconductor device manufacturing discharged to POTW's (publicly owned treatment works) or surface waters on a national basis is estimated to be 628 million liters per day. An average plant's process water flow is estimated to be 2.44 million liters per day. Due to the high purity requirements of the semiconductor manufacturing industry, few plants recycle their water, although up to 80 percent recycle is possible. The principal constituents of the liquid waste streams from semiconductor device manufacturing are suspended solids, fluorides, dichlorobenzene, trichlorobenzene, trichloroethane, and phenols. Values of pH in the range of 2 to 3 are characteristic of the wastes as a result of the acid cleaning and etching. A range of constituent concentrations found in end-of-pipe raw liquid waste streams from semiconductor device manufacturing is shown in Table 2-6.[3] Waste stream suspended solids are comprised primarily of metals from metal film deposition and semiconductor debris that is generated during cutting and surface smoothing processes. Fluorides are primarily the result of cleaning and surface etching processes utilizing weak and concentrated forms of hydrofluoric acid. The large amount of chlorinated hydrocarbons and, to a lesser extent, phenols present in the waste stream comes from solvents and detergents used in the numerous chemical cleaning steps, as well as resist developing and stripping.

The liquid wastes from semiconductor device manufacture may be controlled using end-of-pipe treatment systems. Adjustment of pH with lime, ammonia, or

TABLE 2-3. WORLD DISCRETE MARKET SHARE ESTIMATES
$ million[8]

Company	Year			
	1976	1977	1978	1979
Motorola	290	315	351	419
Philips	220	234	266	290
Texas Instruments	234	227	242	260
Toshiba	146	152	212	242
Siemens	120	135	186	206
Hitachi	147	152	206	284
Nippon	161	182	219	195
Matsushita	137	132	168	134
General Electric	107	109	111	126
RCA	91	98	113	124
Fairchild	103	99	105	116
AEG Telefunken	43	71	88	107
Others	1,107	1,253	1,357	1,567
Total Market	2,906	3,159	3,624	3,990

TABLE 2-4. SOME MANUFACTURERS OF DISCRETE SEMICONDUCTORS[8].

	Amperex	Atlantic Semiconductor	Codi Semiconductor	Collmer Seminconductor	Fairchild	Power Semiconductor	General Diode	General Semiconductor (GSI)	General Transistor (GTC)	Intercomp Corporation	International Components Corporation	International Rectifier	National Semiconductor	Power Components	Semtech	Siemens	RSM Sensitron	Semikron	Solitron	Teledyne Semiconductor	Unitrode Corporation	Thor	Varian
General Purpose Diodes		X	X		X		X		X	X	X	X		X	X		X	X	X		X	X	
Zener Diodes			X	X	X		X	X		X	X				X	X					X	X	
Field Effect Transistors (FFT's)									X	X			X						X	X		X	
Silicon Rectifiers (SCR's)	X					X	X		X	X	X	X				X		X	X		X	X	X
Selenium Rectifiers										X												X	
Thyristors	X					X	X		X	X		X				X		X			X	X	X
Transistors, RF, Microwave	X						X		X	X			X			X						X	
Transistors, Small Signal and Power	X						X	X	X	X		X	X			X			X	X	X	X	
Silicon Rectifiers	X	X	X	X			X		X	X		X		X	X		X	X	X		X	X	X
Silicon Diodes		X	X	X		X	X			X	X	X		X	X	X	X	X	X		X	X	
Power Transistors	X					X	X	X	X	X			X			X	X		X	X	X	X	
VMOS Transistors																X			X			X	
Germanium Transistors							X		X	X												X	
Gate Turnoff Transistors	X					X													X			X	
MOSFET Power Transistors												X				X							
Small Signal Transistors					X															X			
Hi-Power Triacs						X						X											
Power Darlingtons																							

TABLE 2-5. NUMBER OF COMPANIES PRODUCING VARIOUS SEMICONDUCTORS AND THE QUANTITY OF SHIPMENTS OF EACH TYPE[6]

Product	Number of companies
SEMICONDUCTORS AND RELATED DEVICES	
Integrated microcircuits (semiconductor networks):	
As reported in Census of Manufactures	108
As reported in Current Industrial Reports MA-36N, Selected Electronic and Associated Products, Including Telephone and Telegraph Apparatus	101
Hybrid integrated circuits, thick film; composed of material deposited by silk screen process on a passive substrate combined with discrete active or passive components	46
Hybrid integrated circuits, thin film; composed of material deposited by vacuum deposition, sputtering, or similar process on a passive substrate combined with discrete active or passive components	24
Hybrid integrated circuits, multichip; circuits not incorporating film techniques. These are ususally combinations of chips, active and/or passive. Discrete package devices may be used for some, but not all of the circuits	16
Monolithic digital integrated circuits:	
Bipolar:	
DTL (diode transistor logic), excluding microprocessors	10
TTL (transistor transistor logic), excluding microprocessors	18
CML/ECL (current mode logic/emitter coupled logic), excluding microprocessors	7
I^2L (integrated injector logic), excluding microprocessors	4
Microprocessors	6
Other bipolar digital integrated circuits, including diode logic, complementary transistor logic, resistor transistor logic, direct couple transistor logic, etc.	10
Metal oxide silicon (MOS):	
Microprocessors	16
MOS memories	21
Other MOS devices	19
Monolithic analog integrated circuits	22
Transistors:	
As reported in Census of Manufactures	48
As reported in Current Industrial Reports MA-36N, Selected Electronic and Associated Products, Including Telephone and Telegraph Apparatus	37
Signal (less than 1 watt dissipation)	23
Power (1 watt or more dissipation)	23

(continued)

TABLE 2-5 (continued)

Product	Number of companies
Diodes and rectifiers:	
As reported in Census of Manufactures	61
As reported in Current Industrial Reports MA-36N, Selected Electronic and Associated Products, Including Telephone and Telegraph Apparatus	41
Signal diodes and assemblies thereof (maximum current 0.5 amps)	13
Semiconductor rectifier/power diodes and assemblies thereof (current rating greater than 0.5 amps)	28
Selenium rectifier	7
Microwave diodes (mixers, detectors, varactors, parametric, harmonic generators, etc.)	17
Zener diodes (voltage regulator and voltage reference diodes)	23
Semiconductor devices, n.e.c., and parts for semiconductors:	
As reported in Census of Manufactures	112
As reported in Current Industrial Reports MA-36N, Selected Electronic and Associated Products, Including Telephone and Telegraph Apparatus	118
Light sensitive and light emitting devices:	
Solar cells	7
Light emitting diodes (LED)	8
Other	22
Other semiconductor devices:	
Thyristors (SCR's, triacs, PNPN diodes)	14
All other semiconductor devices	15
Semiconductor parts:	
Semiconductor devices and circuits: chips (DICE) and wafers (DISCS)	26
All other semiconductor parts (headers, packages, heat sinks, other accessories, etc.)	75

TABLE 2-6. CHARACTERISTICS OF RAW WASTE STREAMS FROM SEMICONDUCTOR DEVICE MANUFACTURING[3]

Parameter	Concentration range, mg/liter	Mean concentration, mg/liter	Industry wide pollutant discharge, kg/day[a]
Antimony	<0.001-0.187	0.021	13.2
Arsenic	<0.003-0.067	0.018	13.2
Beryllium	<0.001-<0.015	0.002	1.9
Cadmium	<0.001-0.008	0.003	1.9
Chromium	<0.001-1.150	0.129	99.9
Copper	<0.005-2.588	0.570	540.7
Cyanide	<0.005-0.01	0.005	3.8
Lead	<0.04-1.459	0.145	61.5
Mercury	<0.001-0.051	0.004	5.7
Nickel	0.005-4.964	0.502	655.6
Selenium	<0.002-0.045	0.021	6.9
Silver	<0.001-0.013	0.005	3.8
Thallium	<0.001-0.012	0.015	11.3
Zinc	0.001-0.289	0.093	46.5
Phenols	<0.002-6.1	0.630	812.6
Oil and grease	ND-20.8	5.058	2,778.3
Total suspended solids	ND-203	31.61	30,470.6
Total organic carbon	ND-80	55.676	17,094.2
Biochemical oxygen demand	9-202	52.768	38,848.1
Fluoride	ND-330	62.0	35,909.0
1,2,4-trichlorobenzene	<0.01-27.1	4.643	257.5
1,1,1-trichloroethane	<0.01-7.7	1.395	928.2
Chloroform	<0.01-0.05	0.015	15.7
1,2-dichlorobenzene	<0.01-186.0	15.972	499.3
1,3-dichlorobenzene	<0.01-14.8	1.450	174.0
1,4-dichlorobenzene	<0.01-14.8	1.341	156.4
1,1-dichloroethylene	<0.01-0.071	0.029	9.4
2,4-dichlorophenol	<0.01-0.017	0.012	9.4
Ethylbenzene	<0.01-0.107	0.021	6.3
Methylene chloride	<0.01-2.4	0.244	276.1
Naphthalene	<0.01-1.504	0.214	19.5
2-nitrophenol	<0.01-0.039	0.024	27.6
4-nitrophenol	<0.01-0.18	0.061	15.1
Phenol	0.014-3.5	0.519	203.5
Di-n-octyl phthalate	<0.01-0.01	0.01	6.3
Tetrachloroethylene	<0.01-0.80	0.122	363.0
Toluene	<0.01-0.14	0.018	33.9
Trichloroethylene	0.007-3.5	0.322	177.1

[a] Flowrate weighted.

ND - Not detected.

sodium hydroxide is common. Segregation and treatment of individual liquid waste streams is also practiced. There are also many commonly used in-line technologies for reducing pollutant concentrations, for reducing wastewater quantities discharged, for reclaiming potential pollutants for reuse, and for reusing water itself. Generally, in-line treatment is an effective method for improving the performance of end-of-pipe treatment systems.

Solid wastes produced during semiconductor device manufacturing include sludges generated during treatment of liquid process wastes and semiconductor debris from polishing wafer surfaces. Suspended particulates typically contain fine semiconductor material and abrasive particles. The semiconductor materials include silicon wafer particles and small amounts of dopant. Sludges primarily contain precipitated calcium fluoride and other precipitates of spent processing chemicals. Sludges may be dewatered and disposed on-site or contract hauled off-site. Metal and chemical recovery from sludges is also practiced on or off-site.

INDUSTRY ANALYSIS

The following industry analysis considers each individual production operation (or series of closely related operations), called here a process, to examine in detail its purpose and actual or potential effect on the environment. Each process is examined in the following aspects:

1. Function
2. Input materials
3. Operating conditions
4. Utilities
5. Waste streams
6. Control technology

As indicated in the Industry Description, there are a large number of types of semiconductors and related devices. Some information was found in the literature on the production methods used for two categories of these components: (1) transistors and diodes, and (2) integrated circuits (IC's) and light-emitting diodes. Figures 2-6 and 2-7 are flowsheets showing the processes used for these devices, as well as their interrelationships and major waste streams.

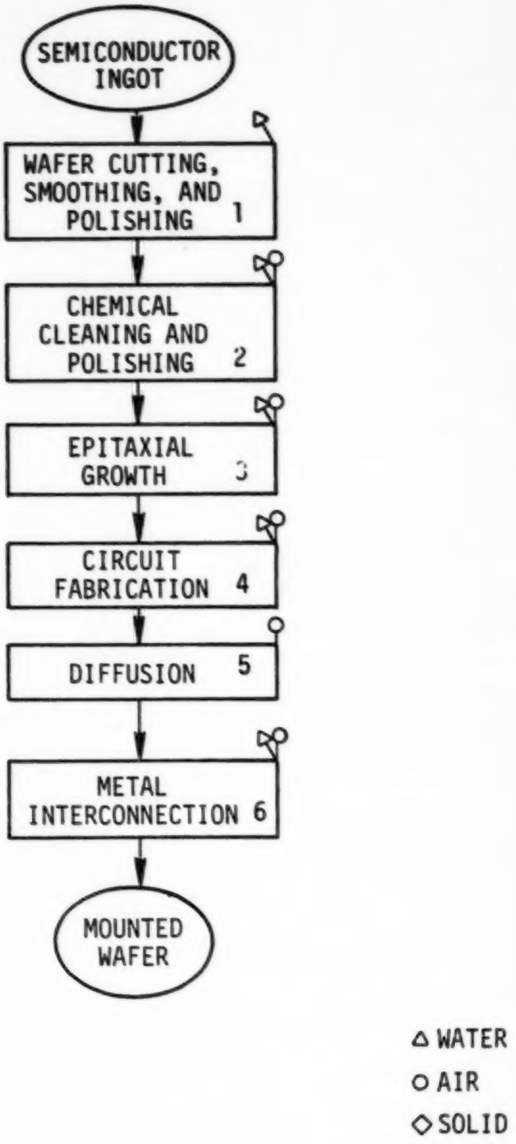
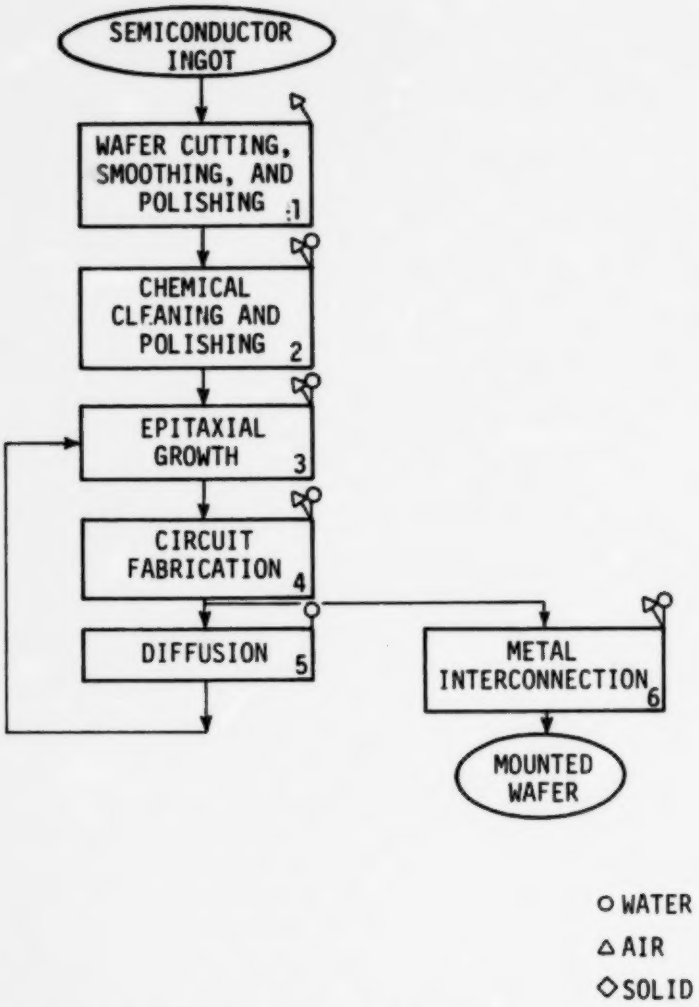

SEMICONDUCTOR INGOT
WAFER CUTTING, SMOOTHING, AND POLISHING 1
CHEMICAL CLEANING AND POLISHING 2
EPITAXIAL GROWTH 3
CIRCUIT FABRICATION 4
DIFFUSION 5
METAL INTERCONNECTION 6
MOUNTED WAFER
△ WATER
○ AIR
◇ SOLID

Figure 2-6. Transistor and diode production flowsheet.


SEMICONDUCTOR INGOT
WAFER CUTTING, SMOOTHING, AND POLISHING 1
CHEMICAL CLEANING AND POLISHING 2
EPITAXIAL GROWTH 3
CIRCUIT FABRICATION 4
DIFFUSION 5
METAL INTERCONNECTION 6
MOUNTED WAFER
○ WATER
△ AIR
◇ SOLID

Note: Process No's. 3 and 4 are repeated up to 20 times for IC's and only once for LED's.

Figure 2-7. Integrated circuit (IC) and light emitting diode (LED) production flowsheet.

Wafer Cutting, Smoothing, and Polishing

1. Function - Semiconductor device manufacturers purchase ingots of doped silicon material or "grow" their own crystals. In either event, the ingot must be sliced into wafers prior to device manufacture. The slice may be circular and range from 1.3 to 10.2 cm in diameter. It may also be trapezoidal or semicircular. After slicing, the wafer is rinsed and smoothed to make both sides flat and parallel. Smoothing is followed by another rinse, polishing, and a final rinse.[3]

Wafer cutting is performed with reciprocating saws, wire saws, rotating (circular) saws, or in some instances ultrasonic cutters. Reciprocating and rotating (circular) saws use an abrasive material such as diamond, boron carbide, silicon carbide, or garnet, which is a component of the saw blade itself. These blades are often operated in the presence of a cooling or lubricating slurry. Circular saw blades attain peripheral speeds of 1500 to 2300 cm/sec when silicon or germanium is cut. These high speeds require that a coolant be injected into the cut to reduce exposure of the blade to excessive heat.[9] Reciprocating saws employ steel blades with a diamond abrasive plating. Wire saws are usually composed of a copper metal alloy. This cutting method often employs the use of an abrasive slurry to perform the actual cutting. The ultrasonic method also achieves cutting through the use of abrasive slurries.

Wafer smoothing consists of either lapping or grinding operations used to remove up to 50 μm of material from the wafer surface. Lapping can remove material from both sides simultaneously, resulting in surfaces which are parallel to within 2.5 μm. Grinders using abrasives can be used to achieve the wafer smoothing. Smoothing is often achieved with a dry abrasive.

Wafer polishing is similar to smoothing, except that it is performed to remove wafer irregularities left behind after the smoothing operation has been completed. Occasionally, hydrochloric acid or sodium hydroxide is used to adjust the pH of the polishing compound.[9] Hydrogen peroxide is added to polishing compounds for germanium polishing.[10]

2. Input Materials - Wafer cutting requires the input of specific semiconductor material to be cut. Types of material include silicon, germanium, gallium arsenide, gallium phosphide, and indium antimonide.[3] Cutting blades may contain diamond, boron carbide, silicon carbide, or garnet abrasives. Wire or ultrasonic cutting systems will employ abrasive slurries containing proprietary solutions. Wafer smoothing requires dry abrasives containing diamond, alumina, zirconia, and chromic oxide. Polishing compounds may be composed of diamond abrasive in an oil suspension. Other compounds may employ water as a liquid carrier. Hydrochloric acid, aqueous sodium hydroxide, or hydrogen peroxide may be added to polishing compounds to adjust for pH.[9,10]

3. Operating Conditions - The steps of cutting, smoothing, and mechanical polishing are all carried out at conditions of ambient temperature and pressure.

4. Utilities - Tap water is used for cooling diamond tipped saws. Deionized rinse water is required following milling operations. Electricity is used to run the mechanical equipment such as saws, lapping machines, and grinders.

5. Waste Streams - There are no air emissions reported for this process.

Wastewater includes cooling water from slicing operations that use diamond tipped saws and from deionized water rinses following slicing, smoothing, and polishing. The wastewaters contain semiconductor particles and abrasive materials from smoothing and polishing. Machining waste stream characteristics for an isolated plant are presented in Table 2-7.[3]

There are no solid wastes other than scrap from cutting and grinding operations.

6. Control Technology - Lime, ammonia, or caustic are typically used for pH adjustment, followed by clarification for solids removal. The settled solids are then collected, dewatered, and disposed on-site or contract hauled for off-site disposal.

TABLE 2-7. SEMICONDUCTOR MACHINING WASTE FOR A TYPICAL PLANT (Flow - 10,409 liter/h)[3]

Pollutant	Concentration, mg/liter
Antimony	0.007
Arsenic	0.003
Beryllium	<0.001
Cadmium	<0.001
Chromium	<0.001
Copper	0.046
Lead	0.001
Mercury	<0.001
Nickel	<0.001
Selenium	<0.003
Silver	<0.005
Thallium	<0.025
Zinc	1.113
Aluminum	0.015
Barium	0.024
Boron	0.222
Calcium	28.040
Cobalt	<0.001
Gold	<0.020
Iron	0.169
Magnesium	13.500
Manganese	0.006
Molybdenum	0.001
Palladium	<0.080
Platinum	<0.050
Sodium	111.601
Tellurium	<0.020
Tin	0.023
Titanium	0.006
Vanadium	0.091
Yttrium	<0.001
Phenols	0.032
Oil and grease	9.0
Total suspended solids	885
Biochemical oxygen demand	310
1,1,1-Trichloroethane	<0.01
1,1-Dichloroethane	0.01
Chloroform	0.02
1,2-Dichlorobenzene	<0.01
Methylene chloride	0.035
Phenol	0.031
Bis(2-ethylhexyl)phthalate	<0.01
Di-N-Butyl phthalate	<0.01
Diethyl phthalate	<0.01

Chemical Cleaning and Polishing

1. Function - Chemical cleaning and polishing are key operations in producing wafer surfaces free of imperfections which might interfere with circuit or device fabrication. Both of these procedures are designed to remove embedded particles and contaminants from wafer surfaces. This is achieved through the use of degreasing solvents to remove organics or acids to remove damaged surfaces. The operations may be assisted through ultrasonic agitation of the bare substrate. Only bare silicon wafers are ultrasonically cleaned. Wafers with semiconductor devices already fabricated on their surfaces will be too frail for such a technique.[9] Following either degreasing or acid treatment, the clean, polished wafers are rinsed in deionized water and blow-dried with air or nitrogen.[11]

2. Input Materials - A typical ultrasonically agitated cleaning bath contains potassium chromate solution or other mildly alkaline solutions such as sodium hydroxide, potassium hydroxide, hydrazine, ethylenediamine, sodium silicates, or sodium hypochlorite. A complexing or chelating agent usually consisting of an alcohol is used to effect dissolution. Alcohols used include isopropanol, n-propanol, sec-butanol, and pyrocatechol. For silicon wafers, acid baths are composed of various mixtures of nitric, hydrofluoric, and acetic acids. For germanium wafers, acid baths are composed of a mixture of hydrogen peroxide and hydrofluoric acid. The most commonly employed cleaning baths for gallium arsenide and gallium phosphide are comprised of bromium-methanol, sodium hydroxide-hydrogen perioxide, sulfuric acid-hydrogen peroxide-water, ammonium hydroxide-hydrogen peroxide-water, or glycerol-hydrochloric acid-nitric acid. High viscosity acid mixtures are preferred for chemical polishing because the preferential reaction results in a leveling action.

3. Operating Conditions - Ultrasonic cleaning is a very rapid process requiring only a few minutes per wafer. Sound vibrations of 20 to 40 kHz are imparted to the cleaning solution. Cleaning solutions are used at room temperature although, in time, ultrasonic agitation will cause the temperature to rise.

The acid baths used in the chemical cleaning operations may be heated as high as 86°C.

4. Utilities - Electricity is used to operate conveyor mechanisms on automated production lines. In addition, ultrasonic agitation is electrically operated. Deionized water is used for rinsing, while compressed air or nitrogen is required for drying.

5. Waste Streams - Air emissions consist of acid fumes from hot acid baths.

Liquid wastes include acid and alkaline contaminated rinse water, spent cleaning solutions, and acid baths. Typically, spent cleaning solution bath dumps are 4 to 7 liters in volume.

There are no solid wastes reported for this process.

6. Control Technology - Acid fumes may be collected by hoods over process baths and sent through ducts to a wet scrubber. The scrubbed air is discharged to the atmosphere, while the acid is contacted with water or some other medium.

The acid contaminated effluent from the wet air scrubber is mixed with spent acid baths, acid contaminated rinsewater, and alkaline cleaning solutions, and finally pH adjusted with lime or sodium hydroxide. The liquid effluent is then sent to a clarifier where acid and alkaline salts settle out and are dewatered prior to contract hauling to disposal.

Epitaxial Growth

1. Function - Semiconductor wafers are inserted into an epitaxial growth furnace (oven) where they receive a polishing etch. A very thin layer (2 to 25 μm) of doped semiconductor is then grown on top of the polished wafer surface. Silicon wafers are subsequently covered with a thin film of silicon dioxide.[12] The techniques by which an epitaxial layer of material is grown on an existing surface fall into two classifications, direct and indirect. Direct techniques involve deposition of the semiconductor on the existing surface directly with no intervening chemical reactions. Direct processes include sputtering, evaporation, and sublimation.

Indirect techniques, which involve chemical and physical interaction of reactants to form the semiconductor in a multistep deposition technique, are used far more often than direct techniques. The indirect technique is performed in either a closed-tube or open-tube system.[11] In a closed-tube system, the substrate and reactants are sealed in a precleaned quartz tube that is under vacuum or filled with an inert gas. The sealed tube is placed in a two-zone oven and heated utilizing radio frequency (RF) induction. The reactants are in the high temperature zone and the wafer is in the lower temperature zone. Germanium and silicon wafers are first treated at high temperatures with a dilute gaseous etchant. Under heat, the semiconductor material reacts with the etchant to produce a highly polished surface prior to epitaxial growth. The reaction rate varies with etchant concentration. Deposition of semiconductor onto the substrate proceeds after stopping the etchant gas flow and starting the flow of the gaseous reactants which starts a "disproportion" reaction. Doping of the film is achieved with predoped reactants.[11]

Open-tube systems are used for "disproportionation" reactions, as well as "decomposition and reduction" reactions. Decomposition and reduction reactors have only one temperature zone. A flat external heater or direct RF heating is used.[9] After epitaxial growth is completed, silicon wafers are exposed to a source of oxygen which causes an oxide film that acts as an insulator to grow on the top surface of the wafer.[12] Process No. 5 presents further details of the open-tube system. Table 2-8 is a summary of methods (open-tube or closed-tube system) for silicon, germanium, and gallium arsenide wafer substrates.[9]

2. Input Materials - For silicon wafer polishing etch, the gaseous mixture used contains hydrogen as the carrier gas with ≤ 1 percent of hydrogen chloride, sulfur hexafluoride, hydrogen bromide, hydrogen iodide, chlorine, hydrogen sulfide, water vapor, or a hydrogen iodide-hydrogen fluoride mixture. Germanium can be polish-etched with anhydrous hydrogen chloride, a mixture of hydrogen iodide in hydrogen, hydrogen sulfide in hydrogen, or water vapor in hydrogen. Epitaxial growth reactants and dopants are all used in gaseous forms. Dopants consist of phosphorus, arsenic, or boron in either of two different compounds. These may be phosphine (PH_3) or phosphorus trichloride (PCl_3), arsine (AsH_3) or arsenious chloride ($AsCl_3$), or boron hydride (B_2H_6) or boron trichloride (BCl_3). Dopants are always diluted with hydrogen (H_2) gas. Reactants for silicon growth are silicon tetrachloride ($SiCl_4$) or silane (SiH_4), which are also diluted with hydrogen. Reactants for germanium growth are germanium tetrachloride ($GeCl_4$) or germanium tetraiodide (GeI_4), and they are also diluted with hydrogen. The reactants for semiconductor growth are mixed with the dopants prior to feeding into the oven. Nitrogen or hydrogen may be used as inert gas prior to or after the epitaxial reactions. After epitaxial growth, oxygen or steam is used as the oxygen source to grow the silicon dioxide film on the top surface of the wafer.

3. Operating Conditions - Etching temperatures are primarily 1050° to 1200°C for silicon and 650° to 910°C for germanium, with a gas flow rate of 9 liters/min. Temperatures in the two-zone oven reach up to 1300°C. The ovens are maintained under a vacuum of 10^{-6} torr. The wafers are heated for several hours.

4. Utilities - Electric power is required for operating vacuum pumps, induction heaters, and control equipment. Inert gas is required for relieving vacuum and diluting dopant gases.

5. Waste Streams - Air emissions consist of excess dopant gases and outgassed dopant from substrate material. In addition to hydrogen chloride vapor from the etchant, hydrogen chloride is also produced as a reaction by-product from the chlorinated compounds that are used.

TABLE 2-8. INDIRECT EPITAXIAL GROWTH TECHNIQUES[9]

Wafer substrate	Method	Reaction	Normal growth temperature, °C	Comments
Silicon	Open tube	H_2 red. of $SiCl_4$	1050-1250	Most widely used
	Open tube	H_2 red. of $SiHCl_3$	1050-1250	Faster growth rates than for $SiCl_4$ system
	Open tube	H_2 red. of $SiBr_4$		Expensive, seldom used
	Open tube	H_2 red. of SiI_4		Expensive, seldom used
	Open tube	Thermal decomposition of SiH_4	1050-1200	Very high deposition rate at reduced pressures, hydrogen only by-product
	Closed-tube disproportionation	$2SiI_2 \rightarrow Si + SiI_4$	450-650	Has been used for very low temperature growth, closed tubes inconvenient to use
	Open-tube disproportionation	$Si + HCl \rightarrow SiCl_4 + \ldots$ $SiCl_4 + H_2 \rightarrow Si + \ldots$	1050-1250	Seldom used intentionally, often occurs on back of slices
Germanium	Open tube	H_2 red. of $GeCl_4$	600-800	Most widely used
	Open tube	Thermal decomp. of GeH_4	500-800	
	Closed-tube disproportionation	$2GeI_2 \rightarrow Ge + GeI_4$	350-450	
Gallium arsenide	Open-tube disproportionation	HCl transport		
	Combination	HCl transport of gallium, reduction of $AsCl_3$		Very commonly used
	Closed-space disproportionation	Water vapor		

Water emissions consist of excess etchant. Process waste characteristics at an isolated plant for quartz tube cleaning are presented in Table 2-9.[5]

There are no solid wastes.

6. Control Technology - The epitaxial furnaces are vented to wet air scrubbers to remove pollutants from the air prior to discharge.

The water from the wet air scrubbers is recirculated. An average bleed-off rate of 35 liter/min discharged to waste treatment has been reported.[3] The bleed-off is performed to reduce scrubber water acidity and pollutant concentrations.

TABLE 2-9. SEMICONDUCTOR PROCESS WASTE FOR AN ISOLATED PLANT[3]

Process	Quartz tube cleaning	Crystal growth scrubbers
Flow (liter/h)	29	2580
Duration (h)	24	24

Pollutant	Concentration, mg/liter	Concentration, mg/liter
Antimony	<0.005	0.017
Arsenic	0.074	0.007
Beryllium	<0.001	<0.001
Cadmium	0.05	<0.001
Chromium	<0.001	0.011
Copper	<0.001	0.007
Lead	0.25	<0.001
Mercury	<0.001	<0.001
Nickel	0.90	<0.001
Selenium	<0.003	<0.003
Silver	<0.005	<0.005
Thallium	<0.025	<0.025
Zinc	0.80	0.059
Aluminum	16.31	<0.001
Barium	0.05	0.026
Boron	60.66	0.164
Calcium[a]	45.92	35.830
Cobalt	0.48	0.003
Gold	0.02	<0.020
Iron	0.46	0.047
Magnesium[a]	23.78	19.080
Manganese	<0.001	<0.001
Molybdenum	0.57	0.004
Palladium	<0.08	<0.080
Platinum	<0.05	<0.050
Sodium[a]	161.57	49.711
Tellurium	0.02	<0.020
Tin	1.01	0.011
Titanium	0.03	<0.001
Vanadium	0.16	0.130
Yttrium	<0.001	<0.001
Fluoride	290	290

[a] Carry through from incoming water.

Note: Analyses not conducted for organics.

Circuit Fabrication

1. Function - Circuit fabrication is actually a series of steps designed to produce images of both devices and circuits on the surface of a wafer. Specific methods used to create and transfer the circuit pattern vary depending on design specifications and overall precision required for the final product. All methods involve use of a photosensitive emulsion called photoresist, or simply resist, that hardens and clings to the wafer surface when exposed to light. Additional information on photoresist materials and processes can be found in Section 6, Printed Circuit Boards.

Adherence of resist to the wafer depends on thorough cleaning of the oxide surface and proper drying to ensure that pockets of solvent are not trapped on the wafer surface. The oxide surface of the wafer is cleaned in alternating baths of alcohol and boiling solvent, followed by a soak in hot acid. Final rinses in alcohol and solvent precede drying. A simple solvent bath will suffice for wafers properly stored prior to the circuit fabrication process. To reduce the probability of trapping solvent pockets, drying is performed by spinning the wafer in the air; this is followed by heating. After drying, a thick coat of photoresist is applied, often using a dropper to distribute resist onto a wafer spinning at high speed. During the spinning, excess photoresist is quickly thrown off by centrifugal force. Resist film thicknesses range between 0.2 and 1.0 μm. The resist then goes through a short drying step followed by baking.[9,11]

Next, a photographic reproduction of the circuit pattern ("photomask") is aligned with the wafer. The resist is exposed for 5 seconds to ultraviolet light through transparent areas of the photomask. Negative-image resist materials polymerize and stabilize upon exposure to ultraviolet light, following which unexposed areas are dissolved away by developer solvent. This leaves resist on the areas of the wafer which were under the transparent areas of the photomask. Positive-image resist materials, on the other hand, are made more soluble by exposure to ultraviolet light. Following resist exposure, developer solvent is used to remove resist material which was under the transparent areas of the photomask.[11,13] For either image transfer method, the remaining resist is spun or blown dry and given a post-development bake. Some processes use another exposure to ultraviolet light instead of baking. Both procedures improve polymerization, adherence, and resistance of the photoresist to subsequent etching. After baking, the wafer is allowed to cool.[9,11]

The wafer oxide surface not protected with resist is then subjected to an acid etch that is completed when the wafer substrate material is exposed. Etching produces depressions in the oxide layer called windows. The windows are holes through which the diffusion of dopants later occurs (Process No. 5). Etch time is determined by oxide thickness and etch rate. Etch rate is a function of acid concentration.[11] After the acid etch, the wafer is rinsed. This is followed by immersing the wafer in resist stripping solution to remove all remaining resist and another rinse. The wafer is then spun or blown dry with nitrogen.[9]

2. Input Materials - The chemicals used to clean the wafer surface are composed of methyl alcohol, methylene chloride, trichloroethylene, and nitric acid. Photosensitive resist is a light sensitive polymer. These polymers are available either as a liquid or dry solid. The nature of these resists is proprietary but they typically contain vinyl cinnamate, quaternary salts, and azide polymers. Developing solutions used to remove soluble resist are generally trichloroethylene, chlorinated hydrocarbons, mixtures of either 10 percent alcohol and 90 percent Stoddard solvent, proprietary commercial developing solutions, or xylene, acetone, ketones, esters, and alkali-based solutions. Etching is carried out using hydrofluoric acid. Resist strippers consist of sulfuric acid and proprietary commercial strippers which contain sulfuric-dichromate, ammoniacal hydrogen peroxide, metachloroperbenzoic acid, or other chemicals.

3. Operating Conditions - For wafer cleaning with trichloroethylene, the cleaning solvent is kept at a gentle boil (~90°C). Nitric acid soaks are performed at 80°C for approximately 20 minutes. No information was found for the operating temperatures of hydrofluoric acid, methyl alcohol, or methylene chloride. Spin drying requires 30 seconds at 2000 to 4000 rpm. Wafer heating to remove solvent uses hot plates at 150°C to 175°C for 1 minute. During resist application, the wafer spins at 4000 to 10,000 rpm for about 1 minute.

Predevelopment drying takes place in a nitrogen box for 15 to 30 minutes or in a dessicator for 1 hour. Predevelopment baking requires approximately 10 to 20 minutes at 85° to 120°C. Developing temperatures range from ambient to 90°C, while developing times range from 30 seconds to 4 minutes. Postdevelopment baking lasts for 10 to 30 minutes at 120°C to 200°C. Commercial resist strippers require approximately 10 minutes, while sulfuric acid requires 20 minutes at 100°C.

4. Utilities - Circuit fabrication is typically automated, requiring electricity to run conveyors and other mechanical equipment. Baking and other heated operations also use electricity to maintain desired temperatures. Deionized water is required for rinsing.

5. Waste Streams - Air emissions consist of organic solvent vapors from wafer cleaning, drying, baking, and developing solvents, as well as fumes of nitric acid, hydrofluoric acid, and possibly sulfuric acid.

Liquid wastes include rinse waters from developing, acid etching, and resist stripping as described in Table 2-10.[3] These wastes contain solvents, acids, and photoresists.

There are no solid wastes from this process.

6. Control Technology - Organic solvent vapors that are produced from cleaning, resist drying and baking, and developing may be collected with fume hoods and conveyed through ducts to a carbon absorption bed. The carbon bed is regenerated with steam and the organic solvents are collected in drums or tanks and hauled off-site for recycling or disposal. Acid fumes may be collected with separate chemical fume hoods and conveyed through ducts to a wet scrubber where they are contacted with water or some other material which will collect the fumes. The scrubbed air then passes on to the atmosphere, and the scrubbing solution is treated along with the other acidic waste streams.

Rinse waters containing developing solvents and resist are routed to one sump where these materials can be collected for recovery or disposal. Disposal methods include incineration or contract hauling. Spent developing solvents are collected and contract hauled. Acidic rinse waters receive pH adjustment using sodium hydroxide or lime followed by sedimentation. The collected solids are then dewatered and hauled away for disposal.

TABLE 2-10. SEMICONDUCTOR PROCESS WASTES FOR THE CIRCUIT FABRICATION PROCESS[3]

Process pollutant	Developer rinse concentration, mg/liter	Etch rinse concentration, mg/liter	Strip resist rinse concentration, mg/liter
Antimony	<0.005	0.005	<0.005
Arsenic	<0.003	0.003	<0.003
Beryllium	<0.001	0.001	<0.001
Cadmium	0.003	0.003	0.001
Chromium	0.004	0.003	0.001
Copper	0.015	0.046	0.019
Lead	0.019	0.161	0.012
Mercury	<0.001	<0.001	<0.001
Nickel	0.057	0.07	0.005
Selenium	<0.003	<0.003	<0.003
Silver	<0.003	<0.003	<0.003
Thallium	<0.025	<0.025	<0.025
Zinc	0.022	0.048	0.032
Aluminum	0.046	5.781	0.031
Barium	0.004	0.011	0.006
Calcium	1.718	2.371	0.258
Cobalt	<0.001	<0.001	<0.001
Iron	0.005	0.149	0.026
Magnesium[a]	0.077	0.142	0.034
Manganese	0.001	0.006	0.001
Molybdenum	0.004	0.019	<0.001
Sodium[a]	0.071	18.315	0.143
Tin	0.023	0.203	0.006
Titanium	0.002	0.036	0.001
Vanadium	0.001	0.081	0.001
Yttrium	0.005	<0.001	0.001
Phenols	0.014	0.016	0.007
Oil and grease	3.0	<1.0	1.0
Cyanide	<0.005	<0.005	<0.005
Total suspended solids	<5.0	31.0	<5.0
Total organic carbon	30	<1.0	<1.0
Biochemical oxygen demand	<4.0	<4.0	<4.0
Fluoride	0.15	875	0.24
Chloroform	0.026	<0.01	0.021
Methylene chloride	0.042		<0.01
Toluene	0.017	<0.01	<0.01

[a] Carry through from incoming water.

Diffusion

1. Function - Dopants are impurities such as boron, phosphorus, and other specific metals introduced into the semiconductor to form both devices and circuits through which electrical impulses are conducted. Diffusion is an evaporative process in which the dopant is heated in a furnace which causes it to reach a gaseous state. The atoms of the dopant bombard the wafer and enter the semiconductor substrate through the "windows" (see Process No. 4) and penetrate to controlled depths to form the lattice of devices within the wafer.[3]

The most commonly used diffusion technique employs the open-tube system. The semiconductor wafers are placed in a heated tube and a continuous flow of inert gas is maintained across the wafer slices during diffusion. Liquid or gaseous dopant sources require a single zone furnace around the tube. The dopant source is either deposited on the surface of the wafer before it enters the tube, or is carried in by the inert gas stream. In the first surface deposition method, a "paint-on" dopant is used in which some evaporable liquid containing the desired diffusing element is applied to the wafer by dipping or spraying. In the second method, a gaseous dopant is added to the flow of inert gas passing through the furnace. Solid dopants require a two-zone furnace around the tube. Solid dopants are heated in the higher temperature zone of the two-zone furnace to a temperature at which there is an appreciable vapor pressure. An inert gas is then used to sweep the vapor into the other zone of the furnace where the diffusion of the dopant into the semiconductor takes place.[11,14]

2. Input Materials - The inert gas carriers are usually argon or nitrogen. Common flow rates for open-tube systems are 0.5 to 5.0 liter/min. When liquid or gaseous dopants are used, oxygen is also introduced into the gas stream at rates of up to several hundred cm^3/min. Table 2-11 shows the dopants used and their physical states at room temperature.[11]

3. Operating Conditions - The semiconductor wafer is heated to between 900° to 1300°C in the furnace. Diffusion times range from 25 minutes to several hours. The temperature ranges of dopants during diffusion are not

TABLE 2-11. COMMON DIFFUSION SOURCES FOR OPEN TUBE SYSTEMS[11]

Dopant source material	Physical state[a]	Temperature ranges,[b]
Commonly used for silicon diffusion:		
As_2I_3	S	170-220
P_2O_5	S	100-300
H_3BO_3	S	
B_2O_3	S	600-1200
Sb_2O_4	S	
Commonly used for germanium diffusion:		
As	S	50-400
Sb	S	300-600
Others:		
P_3N_5	S	500-1000
In	S	550-700
P	S	150-350
$POCl_3$	L	0-40
PCl_3	L	
PBr_3	L	170
$AsCl_3$	L	
BCl_3	L	Room temperature
BBr_3	L	0-30
Ga	L	600-900
PH_3	G	Room temperature
AsH_3	G	Room temperature
B_2H_6	G	Room temperature

[a] S-solid, L-liquid, G-gas (at room temperature).

[b] Dopant source during diffusion, °C.

necessarily the same as the wafer. Dopant temperatures are shown in Table 2-11.[11]

4. Utilities - Furnaces are heated directly or indirectly by electricity. Inert gas is also required for diffusion.

5. Waste Streams - Inert gases (argon or nitrogen) contaminated with dopant gases are vented from diffusion furnaces. The contaminant dopant gases are listed in Table 2-11.[11]

There are no process liquid or solid wastes.

6. Control Technology - Diffusion furnaces may be vented to the same wet scrubbers as the epitaxial growth furnaces (Process No.'s 3 and 4) to remove pollutants from the gas stream prior to discharge. The water from the scrubbers is recirculated, with an average bleed-off rate reported to be 35 liter/min discharged to the plant waste treatment system.[3]

Metal Interconnection

1. Function - A thin metal film is deposited onto the wafer surface to provide contact points for final product assembly and to electrically connect two or more doped semiconductor layers that make up a circuit. One of two methods is commonly used to effect this metallization, sputtering or evaporation.[3,14] In sputtering, the metal charge and precleaned wafer are mounted in a vacuum system. An electron beam bombards the metal charge directly without heating anything else. A small puddle of metal is melted in the center of the surface of the charge and emission takes place from its surface. The metal then collects on the wafer surface. Evaporation is somewhat similar to sputtering, but the metal charge is heated by a hot filamet. When the process is completed and the wafer has cooled, the vacuum is relieved and the wafer is removed.[3,9,11]

The metal charge and the wafers to be coated are thoroughly cleaned prior to metallization. The filament used in evaporation is degreased in hot solvent. The metal charge and wafers are each cleaned in a dilute acid, rinsed in deionized water, and blown dry with nitrogen.[3,9,11]

For either method, the entire surface of the wafer is coated with resist after it is covered with a thin layer of metal. This is followed by a preexposure bake. The wafer is aligned with the proper photomask and exposed to ultraviolet light. Resist is developed using a developer solvent, and unexposed resist is then washed away. Both positive and negative image transfer methods may be used (see Process No. 4). This is followed by drying and another baking. The metal film that is not protected with resist is etched away in an acid bath, and the wafer is rinsed and dried. Resist remaining after etching is removed by immersing the wafer in a resist stripping solution, which is followed by a water rinse, a hot alcohol soak, a cold alcohol rinse, and a final drying. Finally, if the metal deposition step was not carried out at high temperatures, the deposited metal undergoes an alloying step to improve metal-semiconductor contact. This alloying involves heating the wafer to a temperature just above the semiconductor-metal eutectic temperature. The effect is a microalloying of the deposited film into the silicon surface with which it is in contact. This step promotes good electrical contact.[9]

The entire metal deposition procedure may be repeated for instances where more than one metal layer is to be deposited. Following metallization, an insulator is deposited which prevents outside contact to the metal films. The finished wafer is then diced and mounted.

2. Input Materials - Aluminum is the most common metallization used. A thickness of 1 μm is deposited for most thin film circuits, while high powered circuits require up to an 8 μm thick layer. Other metals used for interconnection include chromium, platinum, and the alloys of chromium-gold, chromium-copper, and tantalum-aluminum. The insulation is mainly silicon oxide. Insulator thickness is regularly 50 μm for all crossovers.[9] Prior to metal film deposition by the evaporation method, tungsten filaments are degreased in trichloroethylene. The metal charge is cleaned with dilute hydrofluoric and phosphoric acid, while silicon wafers are also cleaned with dilute hydrofluoric acid.[9,10] Photosensitive resists are described in Process No. 4. The primary etchant used to remove metal films is a mixture which contains 85 percent phosphoric acid, 70 percent nitric acid, and deionized water in a ratio of 10:1:2.5 (by volume). Some use is also made of potassium hydroxide solutions for electrochemical etching.[10] Commercial resist strippers may be used alone or mixed with methylene chloride in a ratio of 1:3. Following the stripper rinse, methyl alcohol is used to aid removal of stripper and to speed drying without leaving a film of residue.[9]

3. Operating Conditions - The vacuum system containing the metal charge and wafer is evacuated to a pressure of 10^{-5} to 10^{-6} torr. When the charge is heated, its vapor pressure reaches 10^{-2} to 10^{-1} torr. Deposition of the metal film occurs at a rate of about 1 μm/sec. Deposit of the sputtered metal occurs on the target (silicon substrate) or within the vacuum containment vessel. No particulate or gaseous emissions are anticipated from a sputtering operation. The silicon wafer is heated to 540° to 575°C for the deposition of aluminum on silicon. After coating the metal, the wafers are resist-coated directly or stored. If stored for any length of time, the wafers are heated for 10 minutes at 150°C before applying resist. During resist application, the wafer spins at 4000 to 10,000 rpm for about 1 minute to disperse the

resist evenly. Pre-exposure baking is performed at 85°C for 10 to 20 minutes. Exposure to an ultraviolet source requires only 5 seconds. Developing involves immersion in several solutions and requires 5 minutes. Post-exposure bake requires approximately 30 minutes at 135°C. Acid etching baths are maintained at 45° to 55°C. Wafers are immersed in the acid until etching is complete as determined by visual observation.

4. Utilities - Electricity is required to heat the metal charge and the wafer, to bake the resist, and to do other process heating. Deionized water is used for rinsing and making up etching solutions. Compressed nitrogen is used to dry the wafer after rinsing.

5. Waste Streams - Air emissions consist of organic solvent vapors from filament cleaning, resist drying, developing solutions, and resist strippers. Acid fumes originate from acid cleaning the metal charge and wafer surface, and from acid etches used to remove metal from unwanted areas of the wafer surface.

Liquid organic wastes include spent baths of developer and resist stripper and rinsewater contaminated with stripper and photoresist. Liquid wastes also include spent acid baths and acidic rinsewater containing dissolved metals, as described in Table 2-12.[3]

Solid wastes from this process are minimal.

6. Control Technology - Organic vapors from cleaning, resist drying, and baking may be collected with fume hoods and conveyed through ducts to a carbon adsorption bed. The carbon bed is regenerated with steam and the solvent is collected for off-site disposal or recycle. Acid fumes may be collected with a separate chemical fume hood and conveyed through ducts to a wet scrubber where they are contacted with water or some other liquid which will remove the fumes. The scrubbed air then passes on to the atmosphere while the scrubber liquid is treated along with the other acidic waste streams.

Rinse water containing developing solvents and resists is routed to one sump where these materials can be collected for recovery or disposal. Disposal methods include incineration or contract hauling. Spent developing solvents are collected and contractor hauled. Acidic rinse waters receive pH adjustment using sodium hydroxide or lime, followed by sedimentation. The collected solids are dewatered and hauled away for disposal.

TABLE 2-12. METAL INTERCONNECTION ETCH RINSE FOR AN ISOLATED PLANT[3]

Pollutant	Concentration, mg/liter
Antimony	<0.002
Arsenic	<0.003
Cadmium	<0.003
Chromium	<0.02
Copper	<0.003
Lead	<0.01
Mercury	<0.001
Nickel	<0.025
Silver	<0.002
Thallium	<0.02
Zinc	0.002
Phenols	<0.01
Cyanide	<0.005
Chloroform	0.066
Methylene chloride	<0.01
Bis(2-ethylhexyl)phthalate	<0.01
Butyl benzyl phthalate	<0.01
Di-N-butyl phthalate	<0.01
Di-N-octyl phthalate	<0.01
Diethyl phthalate	<0.01
Toluene	<0.01

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SECTION 3

CAPACITORS

INDUSTRY DESCRIPTION

Capacitors are electronic devices that are basically used for the storage of electrical energy, although depending on their characteristics, they may serve in various other functions. Major applications include the following:[1]

- Energy storage elements - to accumulate electrical energy at one rate and to discharge it at a faster rate; typical examples are motor starting capacitors, fluorescent lamp ballasts, and automotive ignition condensers.
- Protective devices - in combination with resistors to reduce radio interference caused by arcing.
- Filtering devices - to distinguish among currents of different frequencies.
- Bypass devices - to prevent the flow of direct current without impeding the flow of alternating current; bypass capacitors attenuate low frequency currents while permitting higher frequency currents to pass.

There are many examples of the latter three applications in electronic and television components, audio equipment, and instrumentation.

A large variety of capacitors are manufactured. The particular application will determine the type and size of capacitor used. Capacitance is a measure of the quantity of electrical charge the capacitor will hold per unit of potential between conductors; it is independent of the potential impressed on the unit.

Two basic types of capacitors are manufactured, fixed and variable. Fixed capacitors are layered structures of conductive and dielectric (i.e., nonconductive) surfaces. The layering is either in the form of rigid plates or thin sheets of rolled flexible material. Fixed capacitor types are distinguishable in terms of type of conducting, dielectric, and encapsulating materials. The major types include:

Paper dielectric
Film dielectric
Metallized dielectric
Dual dielectric
Tantalum dry slug and wire
Tantalum foil
Tantalum wet slug
Aluminum electrolytic
Mica dielectric
Ceramic
Glass encapsulated

Variable capacitors are larger versions of fixed capacitors with provisions for adjustment of plates separating the dielectric. They serve two basic functions, tuning and trimming. The two types of tuning capacitors are air dielectric and semi-conductor voltage-variable (varactors).[2] Trimming capacitors are small-value adjustable capacitors usually used in parallel with the larger-value tuning or fixed capacitors to make fine adjustments of total capacitance in a circuit. These are classified by the dielectric used into such categories as air, mica, ceramic, glass, and plastic.[2]

Raw Materials

The raw materials for capacitors include conductors, dielectrics, electrolytes, leads, and encapsulating materials:[1,2]

- Conductors - High-purity aluminum foil is used extensively in several types of fixed capacitors, as aluminum is an excellent conductor and is relatively inexpensive compared with other conductive materials. Tantalum foil and tantalum sintered metals are also used. This material is relatively expensive, but because of its durability and electrical stability, is often used in miniature and subminiature capacitor applications. Other foils used less often include tin-lead, tin, brass, and copper. Numerous types of precious metal inks or pastes serve as conductors in layered monolithic capacitors; because of their expense, they constitute a significant portion of miniature and subminiature costs. Conductors in variable capacitors are usually aluminum plates, but brass and copper are also used. Brass and copper plates may be plated with silver to increase surface conductivity or with nickel or cadmium to prevent corrosion.

- Dielectrics - Dielectrics may be solids, liquids, or gases, or combinations chosen to take advantage of various electrical characteristics. Ceramic capacitors use solid ceramic dielectrics which display exceptional dielectric and thermal properties that increase their durability and reliability. They are also relatively inexpensive. Ceramic materials are usually mixtures of complex compounds such as barium titanate, calcium titanate, strontium titanate, and lead niobate. Mixtures of fine ceramic powders and resins are used in monolithic ceramic capacitors.

Kraft paper, glass cloth, and plastic film are used as dry dielectrics and are relatively inexpensive but are not as useful in high-voltage (above 1000 volts) applications as are mica, low-loss ceramic, or oil-soaked paper dielectrics. Glass cloth materials also exhibit good dielectric loss and insulation resistance. Phenolic resins are often used to impregnate paper dielectrics, whereas silicone, melamine, and epoxy resins are used with glass cloth. Plastic film dielectrics include polyester (polyethylene pterapthalate), polysulfone, Teflon, and polyimide. Both paper and plastic dielectrics may be metallized with aluminum or zinc.

Glass and mica are excellent dielectric materials and, although relatively inexpensive, require special skills and equipment for efficient handling. Mica may also be coated with a silver oxide oil paint by silk-screening or spraying methods. This paint is fired to reduce the film to pure metallic silver. Electrochemically-formed oxide coatings are used extensively as dielectrics in higher quality aluminum electrolytic, tantalum foil, and tantalum slug capacitors. These coatings provide exceptional dielectric properties.

- Electrolytes - Electrolytic capacitors usually use a liquid electrolyte and an oxide film as the dielectric. The kraft paper also serves as a spacer and an absorbing medium for the electrolyte. The electrolyte is usually less than a one percent solution of strong acids, glycols, and salts dissolved in deionized water. Acids used in wet-slug tantalum capacitors include sulfuric acid and lithium chloride.
- Leads - Copper and tantalum are the most common materials for capacitor leads. Capacitors that are used on printed circuit boards often do not have leads but are attached directly to the board.
- Encapsulating materials - Steel and aluminum containers, phenolic moldings, and epoxy moldings are the most common encapsulating materials for fixed capacitors. Wax and various other plastics are used to seal metal capacitor containers. Glass encapsulation is also used. Ceramic and brass are used as enclosures for variable capacitors.

Products

The Bureau of the Census classifies fixed and variable capacitors into SIC 3675. Varactors are classified with semiconductors (SIC 3674) and are not discussed in this section.

Capacitor sales by U.S. companies exceeded $1 billion for the first time in 1979, an increase of nearly 20 percent over the previous year.[3] Due to the recession, however, the overall growth rate is expected to decrease in 1980 and 1981.

According to one report, aluminum electrolytic capacitors will be among the hardest hit in the near future due to their heavy use in consumer items in the automotive and entertainment markets.[3] However, they are becoming increasingly attractive for other applications, due to their reduced size, improved performance characteristics, lower price, and wide availability. It is predicted that in low impedance applications, where aluminum capacitors are particularly suitable, tantalum capacitors may lose up to 60 percent of their market share.[3] A major factor is the rising cost of tantalum, which has increased sixfold in the past five years to about $550 a kilogram. Tantalum ore is in short supply, and the mineral is presently mined in only three regions: Africa, South America, and Canada. It is reported that there is little likelihood of new mines opening because costs are too high for the expected return. Reworking slag heaps is also not a promising prospect.[3]

Although new film capacitors are not expected to increase in sales to any great extent in the near future, new processing techniques already developed and improvements in manufacturing and packaging techniques yet to come should keep prices of these capacitors down. With the prices of aluminum, tantalum, and ceramic caps rising, films are becoming more attractive. Film capacitors are also more amenable to automation than aluminum electrolytics, thus allowing price reductions when made in large quantities. They are expected to penetrate several new markets, particularly in high-frequency and high-current applications.[3]

Monolithic ceramic chip capacitors are the fastest growing segment of the industry. It is expected that their production will further increase upon introduction of automatic chip insertion equipment. These capacitors find a wide variety of applications, but are used particularly in computers and associated peripherals. Since these applications do not show significant signs of weakness, the demand for these capacitors remains strong.[3]

Mica capacitors are expected to suffer due to high metal costs. Silver, which amounts to a significant part of total materials cost in mica capacitors, increased in cost sharply in early 1979, though it has come down somewhat since.[3]

Table 3-1 provides details of the sales of major capacitor types over the past 10 years.[3] Figure 3-1 shows the changes over the past decade in sales for each major type of capacitor.[3] A summary of forecasted sales for 1980 and 1983 is given in Table 3-2.[4]

Companies

According to the 1977 Census of Manufactures, there are approximately 118 plants which produce capacitors, including oil-filled capacitors (which are not included in SIC 3675).[5] The number of companies involved in production of the various types of capacitors is presented in Table 3-3.[5] The size of these establishments based on total employment is presented in Table 3-4.[5]

There are four major producers of tantalum capacitors: Kemet of Greensville, South Carolina, with a 40 percent share of the market; Sprague Electric of North Adams, Massachusetts, 38 percent; and Mepco/Electra of Morristown, New Jersey, and P. R. Mallory & Co., of Indianapolis, Indiana, 7 percent each.[3]

There are two major producers of mica capacitors: Cornell-Dubilier Electric of Newark, New Jersey, with a 50 percent share of the market; and Sangamo Weston of Pikens, South Carolina, with 40 percent.[3]

Table 3-5 shows the market share of companies manufacturing monolithic ceramic capacitors. By far the largest is AVX Ceramics, which has almost a third of the market.[3]

There are three major manufacturers of aluminum capacitors. Sprague is the largest, with a 45 percent share of the market, and Mallory and Mepco/Electra each have 20 percent. The remaining 15 percent of the market is reportedly filled by foreign suppliers.[3]

Environmental Impacts

The capacitor manufacturing industry includes a number of capacitor types, a variety of production methods, varying degrees of manufacturing automation, and facilities ranging in size from those with only a few workers to those with hundreds or even thousands of employees.[5] There thus may be considerable variation in the discharges that are produced at various facilities, even those which manufacture the same type of capacitors.

TABLE 3-1. CAPACITOR SALES OVER PAST 10 YEARS[3]

Millions of units

	Year									
	70	71	72	73	74	75	76	77	78	79
Paper and film	542	570	496	666	591	396	474	582	662	621
Tantalum	285	272	364	564	610	353	526	637	786	899
Aluminum	204	208	234	312	296	149	195	201	202	205
Mica	173	173	208	278	254	135	164	201	b	b
Ceramic	1,376	1,757	2,113	2,646	2,180	1,659	2,822	3,451	3,614	4,371
Other fixed	49	49	63	79	63	37	62	49	198[a]	7
Variable	50	55	71	103	57	53	62	57	61	53
Total	2,678	3,084	3,609	4,648	4,032	2,781	4,305	5,179	5,523	6,156

Millions of dollars

	Year									
	70	71	72	73	74	75	76	77	78	79
Paper and film	185	153	104	138	139	94	129	160	205	214
Tantalum	101	81	91	135	162	108	132	156	188	262
Aluminum	82	77	88	118	137	83	111	128	151	185
Mica	20	22	22	31	34	22	24	24	30	b
Ceramic	75	82	106	154	173	139	185	241	289	352
Other fixed	9	7	9	11	13	11	12	13	43	12
Variable	12	12	19	27	19	14	16	16	20	26
Total	483	435	438	612	676	470	608	744	897	1,050

[a] Includes mica.

[b] No data available.

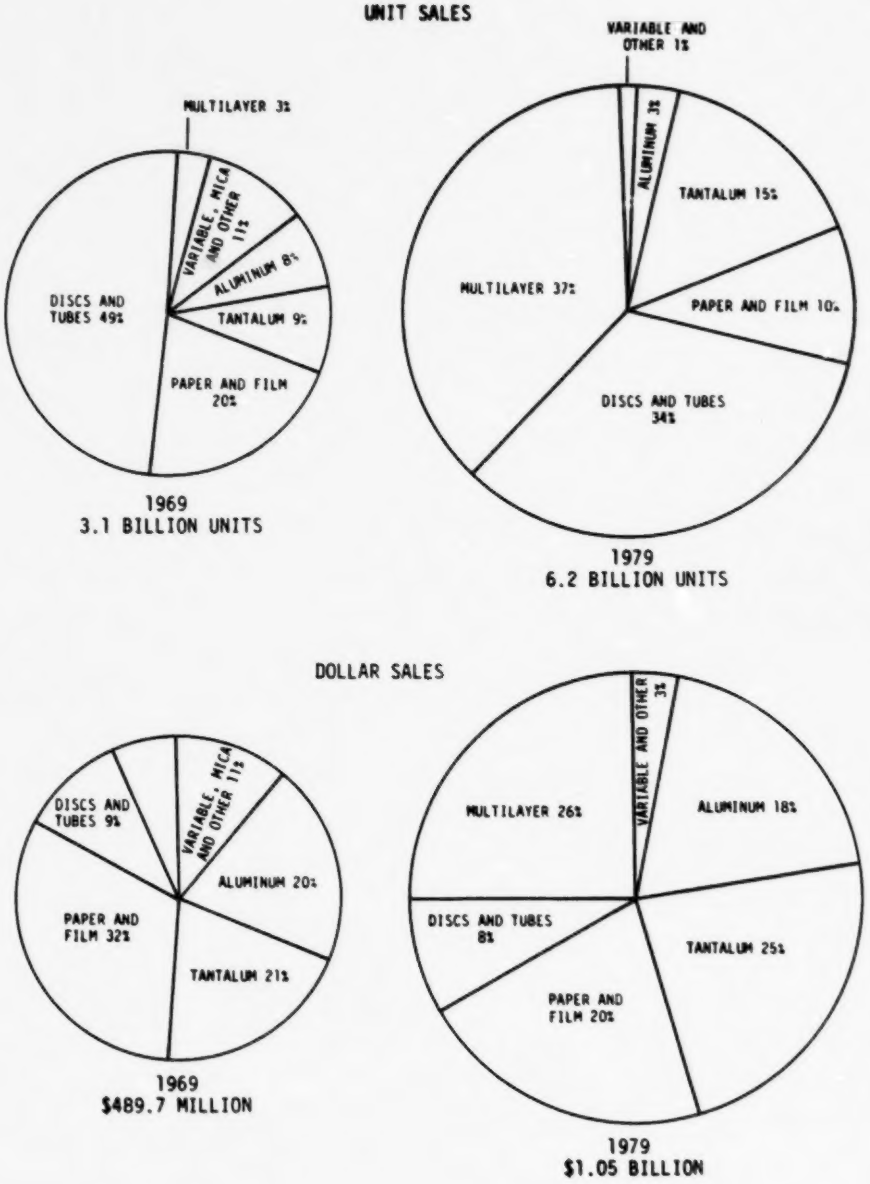

Figure 3-1. Capacitor sales: A comparison of growth over the past decade.[3]

TABLE 3-2. FORECAST FOR CAPACITOR SALES, $ MILLION[4]

Capacitor type	Quantities		Annual growth %
	1980	1983	
Al electrolytic capacitors	200.0	220	5.7
Tantalum capacitors	177.8	215	5.6
Paper capacitors	90.4	98	2.4
Film capacitors	115.0	123	0.8
Ceramic capacitors except chip	364.4	509	13.1
Ceramic chip capacitors	50.3	78	15.1
Mica capacitors	35.5	36	1.4
Variable dielectric capacitors	29.0	34	5.3
Glass and porcelain capacitors	5.2	4	-7.2

TABLE 3-3. NUMBER OF COMPANIES MANUFACTURING VARIOUS CAPACITOR TYPES[5]

Capacitor type	No. of companies
Paper dielectric:	
Metal case	20
Nonmetal case	8
Film dielectric, metal and nonmetal case	30
Metalized dielectric:	
Metal case	11
Nonmetal case	11
Dual dielectric, metal and nonmetal case	23
Tantalum electrolytic:	
Slug and wire solid dry electrolytic:	
Metal case, hermetic	6
Metal case, nonhermetic	7
Nonmetal case	11
Foil and wet slug electrolytic	8
Aluminum electrolytic:	
Metal case tubular:	
Standard (6/8-inch diameter)	9
Standard (under 5/8-inch diameter)	8
All others	9
Mica dielectric, fixed	9
Ceramic dielectric:	
Fixed tubular, disc, plate, stand-off tubular and disc, and all two-thermal ceramic devices	9
Monolithic:	
Chips	19
Leaded-radial	22
Leaded-axial	14
Other	5
All other fixed	8
Variable air dielectric, mica, ceramic, and glass dielectric	16

TABLE 3-4. SIZE BREAKDOWN OF CAPACITOR PRODUCERS BASED ON TOTAL EMPLOYMENT[5]

Average employee range	Number of establishments
1-4	7
5-9	3
10-19	11
20-49	20
50-99	11
100-249	32
250-499	15
500-999	16
1000-2499	2
2500 or more	1

TABLE 3-5. MAJOR MONOLITHIC CERAMIC MANUFACTURERS[3]

Company	Location	Market share, %
AVX Ceramic, affiliate of AVX Corporation	Myrtle Beach, SC	32
Kemet, affilliate of Union Carbide Corporation	Greensville, NC	17
Centralab Electronics Div., Globe Union Inc.	Milwaukee, Wisconsin	9
Sprague Electric, subsidiary of General Cable	North Adams, MA	8
San Fernando Electric Mfg. Co., subsidiary of West-Cap Arizona	San Fernando, CA	8
Corning Glass Works, Corning Electronics	Corning, NY	7
Vitramon, Inc.	Bridgeport, CT	7
All other companies		11

The only reported sources of air emissions from capacitor production are metal fumes from soldering and possible organic vapors from paint drying and use of molten epoxy and phenolic compounds. The use of specific controls is not reported in the literature examined.

Liquid effluents generally consist of weak acidic solutions and rinse and cooling waters. The production of glass encapsulated capacitors results in discharge of fluorescent penetrating solutions. Stronger acidic solutions, which may contain dissolved metals, are released from etching operations at aluminum electrolytic capacitor plants. None of these effluents represent a particular treatment problem, and most are discharged directly to municipal treatment systems. Pretreatment of the effluents (e.g., sand filtration or settling) is employed at some facilities before being released into municipal systems.

There are no significant sources of solid waste from capacitor manufacturing.

INDUSTRY ANALYSIS

The following industry analysis considers each individual production operation (or series of closely related operations), called here a process, to examine in detail its purpose and actual or potential effect on the environment. Each process is examined in the following aspects:

1. Function
2. Input materials
3. Operating conditions
4. Utilities
5. Waste streams
6. Control technology

Some information was found in the literature on the production methods used for six distinct capacitor types: tantalum wet and dry slug, tantalum foil, glass encapsulated, aluminum electrolytic, ceramic, and mica. Each is discussed separately in the following analysis. Figures 3-2 to 3-6 are flowsheets showing the processes used for the first four of these capacitor types, as well as their interrelationships and major waste streams.

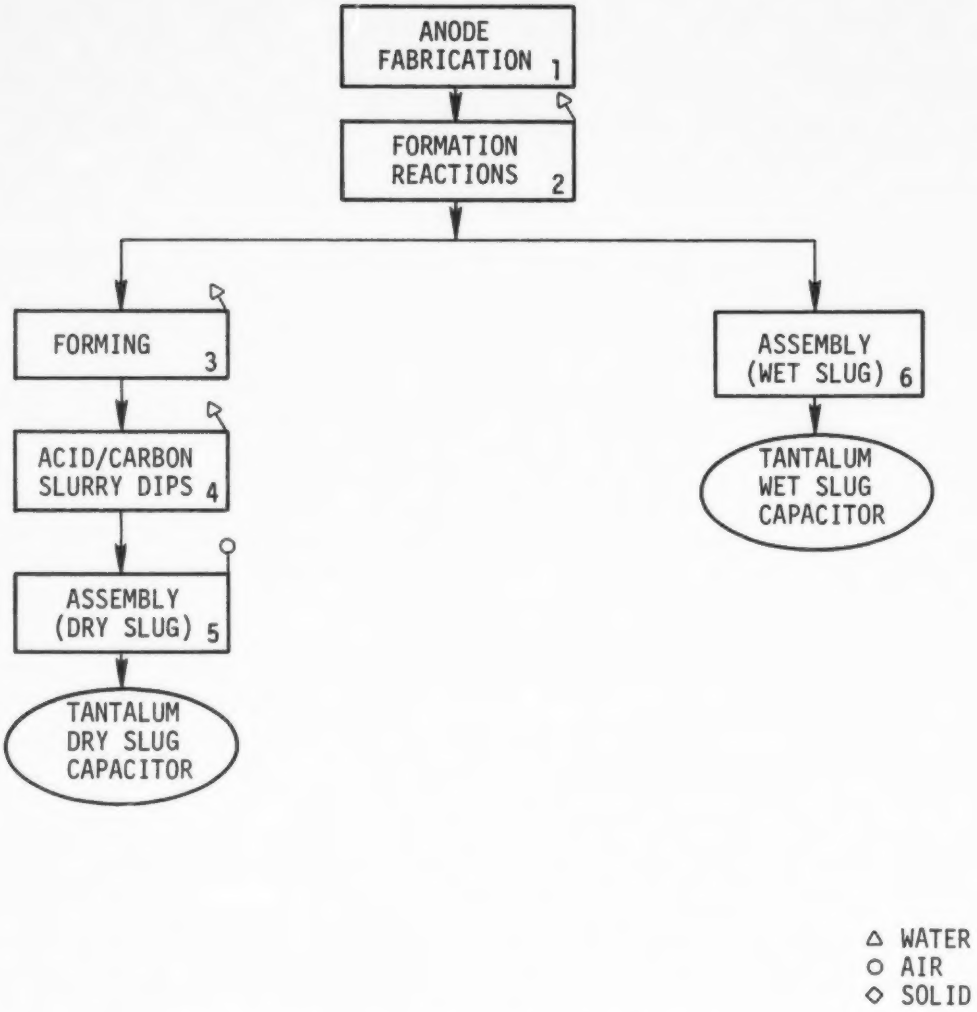
ANODE FABRICATION 1
FORMATION REACTIONS 2
FORMING 3
ACID/CARBON SLURRY DIPS 4
ASSEMBLY (DRY SLUG) 5
TANTALUM DRY SLUG CAPACITOR
ASSEMBLY (WET SLUG) 6
TANTALUM WET SLUG CAPACITOR
△ WATER
○ AIR
◇ SOLID

Figure 3-2. Tantalum wet and dry slug capacitor production flowsheet.

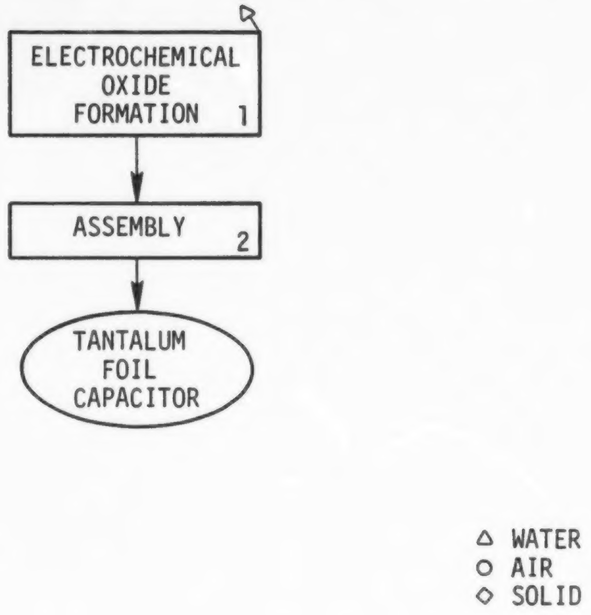
ELECTROCHEMICAL OXIDE FORMATION
1
ASSEMBLY
2
TANTALUM FOIL CAPACITOR
△ WATER
○ AIR
◇ SOLID

Figure 3-3. Tantalum foil capacitor production flowsheet.

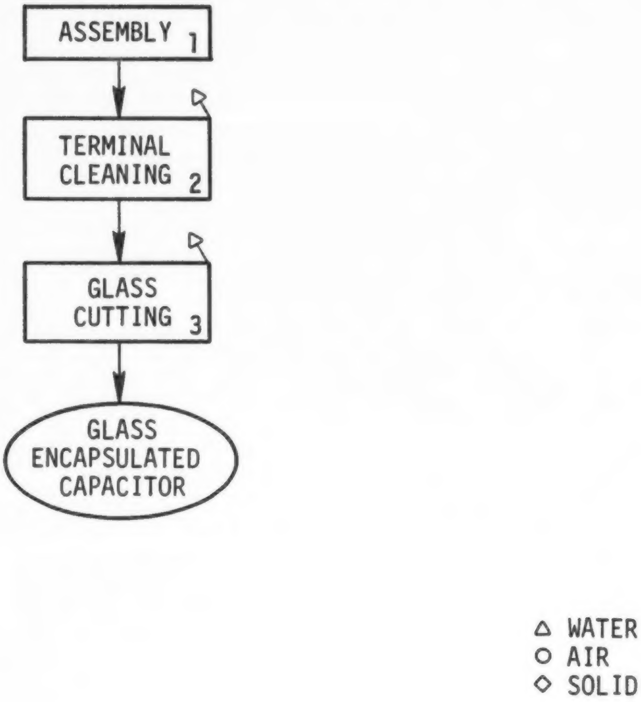
ASSEMBLY 1
TERMINAL CLEANING 2
GLASS CUTTING 3
GLASS ENCAPSULATED CAPACITOR
△ WATER
○ AIR
◇ SOLID

Figure 3-4. Glass encapsulated capacitor production flowsheet.

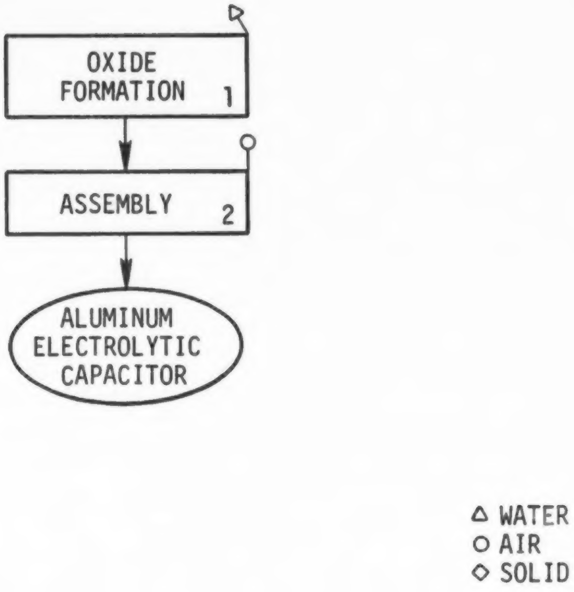
OXIDE FORMATION
1
ASSEMBLY
2
ALUMINUM ELECTROLYTIC CAPACITOR
△ WATER
○ AIR
◇ SOLID

Figure 3-5. Aluminum electrolytic capacitor production flowsheet.

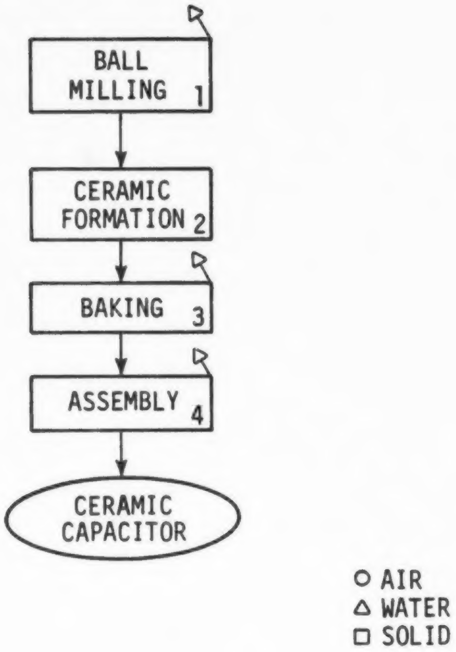
BALL MILLING 1
CERAMIC FORMATION 2
BAKING 3
ASSEMBLY 4
CERAMIC CAPACITOR
○ AIR
△ WATER
□ SOLID

Figure 3-6. Ceramic capacitor production flowsheet.

The lack of information on the production of mica capacitors precludes a complete assessment of this process sequence in the IPPEU format. The dielectric fabrication operation is briefly described, but the sequence of subsequent steps in the process is unclear from the descriptions in the literature. Similarities have been reported to the manufacture of both glass encapsulated and layered ceramic capacitors.[1] The IPPEU description of the dielectric fabrication process of mica capacitor production is included in this draft; however, subsequent steps are not characterized.

Anode Fabrication

1. Function - Tantalum powder is combined with an organic binder and pressed into a pellet on a tantalum lead wire. The pellets are heated in a vacuum furnace to produce a sintered tantalum slug.

2. Input materials - Tantalum powder and wire are the primary input materials in the production of the sintered tantalum slug. An organic binder (of unknown composition) is added to the tantalum powder to allow it to be compressed into a pellet. Specific quantities for these inputs are not available.

3. Operating Conditions - The temperature and pressure of the vacuum furnace are not known. All other steps in this process (i.e., mixing, pelletizing) are performed at ambient conditions.

4. Utilities - The heating elements and vacuum pump of the furnace are electrically controlled. There are no other utility requirements.

5. Waste Streams - There are no air, water, or solid wastes reported for this process.

6. Control Technology - The use of controls for this process is not discussed in the literature.

Formation Reactions

1. Function - An oxide film must be formed which will serve as the dielectric for the capacitor. The sintered tantalum slugs are dipped into a dilute acid solution to form a thin tantalum oxide film. This reaction proceeds rapidly and the sintered tantalum slug is then rinsed with deionized water and air dried. The product of these formation reactions is tantalum slug anodes that are further treated to form either wet or dry slug capacitors.

2. Input Materials - The acids used in the dilute acid bath are nitric and phosphoric. The concentration of the acid solution is not known. The only other input material to this process is deionized water used to rinse the sintered tantalum slug.

3. Operating Conditions - The acid oxidation and rinse steps are performed under ambient conditions of temperature and pressure.

4. Utilities - Water is used to dilute the acid and rinse the tantalum slugs of any acid residue. Electricity powers the automated equipment. Specific quantities are not available.

5. Waste Streams - There are no air emissions reported for this process.

A small wastewater stream results from this process. It consists of batch dumps of very weak acid solutions and deionized rinse water. The quantity is reported as 38 liter/h at one plant.[1]

There are no solid wastes from this process.

6. Control Technology - Special wastewater control procedures are not employed. Effluent streams are discharged directly to the general municipal sewer or the surface.

Forming

1. Function - An additional oxide coating is desirable in the production of dry slug capacitors. Sintered tantalum oxide coated pellets are dipped into a viscous solution of manganese nitrate and then placed in a heated atmosphere with steam. A manganese oxide coating develops on the tantalum oxide coating.

2. Input Materials - Manganese nitrate is the input material for this reforming process. The solvent used in the manganese nitrate solution is not known. Steam is used presumably to provide a humid atmosphere.

3. Operating Conditions - Operating conditions for the reforming process are not available.

4. Utilities - The source of energy used to generate the steam for this process is not reported.

5. Waste Streams - There are no air emissions associated with this process other than steam.

The process has a very low discharge of manganese nitrate solutions, estimated at 19 liter/h for one plant.[1] No other effluents are associated with this process, except water condensate.

There are no solid wastes from this process.

6. Control Technology - Observed wastewater control technologies include settling and contract hauling of sludge.[1]

Acid/Carbon Slurry Dips

1. Function - Coated pellets intended for dry slug capacitors are dipped into a dilute acid solution to eliminate any defects in the oxide coatings. They are then rinsed with deionized water, dipped into a carbon slurry, and air dried.

2. Input Materials - Nitric and phosphoric acids are used in this process. The acid is diluted with deionized water; the final concentration is unavailable. The composition of the carbon slurry is unknown, as are the quantities of input materials used.

3. Operating Conditions - These dipping operations are performed at ambient conditions.

4. Utilities - Water is used to dilute the acid and rinse the manganese oxide-coated slug of any residual acid.

5. Waste Streams - There are no air emissions.

There is a wastewater discharge which consists of batch dumps of the dilute acids and deionized rinse water.

There are no solid wastes from this process.

6. Control Technology - No wet treatment systems are used for this process. Wastewater is discharged directly to municipal sewers or the surface.

Assembly (Dry Slug)

1. Function - The dry tantalum slug anodes are coated with a special silver paint which becomes the cathode. Another tantalum lead wire is soldered to the coating to electrically complete the capacitor. The capacitor is dipped into a molten epoxy or phenolic compound and air dried. The capacitor is then electrically evaluated and shipped.

2. Input Materials - The composition of the special silver paint that comprises the cathode is unavailable and is probably proprietary. Other inputs include tantalum wire, an epoxy or phenolic compound used to coat the capacitor, and the solder used to attach the tantalum lead wire to the cathode coating. Specific quantities for these inputs are not available.

3. Operating Conditions - All assembly processes are presumably performed under ambient conditions.

4. Utilities - Electricity is used to operate the automated assembly and testing equipment and generate the heat for soldering.

5. Waste Streams - Potential air emissions include metal fumes from soldering operations and organic vapors from air drying paint or the molten epoxy or phenolic compounds.

There are no liquid or solid waste streams generated by this process.

6. Control Technology - Controls used in this process, if any, are not reported in the literature.

Assembly (Wet Slug)

1. Function - Tantalum slugs used in wet capacitors receive no further treatment after the formation reactions. The sintered tantalum slug with an oxide coating is inserted into a silvered metal can (the cathode), filled with an electrolyte, and sealed. The unit is then electrically evaluated and shipped.

2. Input Materials - The base composition of the silvered metal can and the chemical composition of the liquid electrolyte are not available.

3. Operating Conditions - The assembly of tantalum wet slugs is conducted at ambient conditions.

4. Utilities - Electricity is the only utility used (i.e., automated equipment, quality control testing).

5. Waste Streams - There are no air, water, or solid waste streams associated with this process, other than possible spills of electrolyte.

6. Control Technology - There are no controls applicable to this process.

Electrochemical Oxide Formation

1. Function - An oxide coating must be developed on the tantalum foil to provide the dielectric of the capacitor. Tantalum foil (usually in strips) is electrochemically reacted with mildly acidic glycol solutions to form this oxide layer.

2. Input Materials - Tantalum foil is the base material, and is typically handled in individual strips or rolls. Other inputs include acidic glycol solutions and water. The chemical compositions of these various solutions are not described in the literature.

3. Operating Conditions - Formation reactions are typically batch dipping operations, performed in open tanks under ambient conditions of temperature and pressure.

4. Utilities - Electricity is used to operate the electrochemical processing equipment.

5. Waste Streams - There are no air emissions from this process.

The oxide formation reaction is the primary water discharging process from tantalum foil capacitor manufacturing facilities. The mass discharge from this reaction is directly proportional to the surface area of foil processed. The wastewater discharge results from batch dumps of acid solutions and subsequent water rinsing. An estimated discharge rate of 115 liter/h has been reported.[1]

No solid wastes are characteristic of this process.

6. Control Technology - Wastewater discharges receive no special treatment and are routed directly to publicly-owned treatment works.

Assembly

1. Function - The dried tantalum foil with oxide coating is layered with kraft paper and sometimes plastic sheets and wound to form a capacitor core. The core is then inserted into a metal container. The containers and cores are placed under heavy vacuum, the vacuum is released, and the chamber is flooded with electrolyte. The capacitors are then sealed, air dried, and electrically aged. The electrical aging improves the integrity of the oxide coating and establishes the equilibrium capacitance of the capacitors. The finished capacitors are electrically evaluated and shipped.

2. Input Materials - Input materials include kraft paper or plastic film which is used as a dry dielectric, a liquid electrolyte, and the metal container which houses the core. Kraft paper serves as a spacer and an absorbing medium for the electrolyte. The electrolyte is usually less than a one-percent solution of strong acids, glycols, and salts dissolved in deionized water. Specific chemical components and the amounts used in electrolyte solutions are not available.

3. Operating Conditions - The capacitor core and housing is placed under heavy vacuum prior to treatment with the electrolyte. All other process operations are performed under ambient conditions.

4. Utilities - Electricity is used to operate the manufacturing and testing equipment and to "age" the electronic components.

5. Waste Streams - There are no air, water, or solid wastes reported to be generated during this process.

6. Control Technology - The use of controls for this process is not discussed in the literature.

Assembly

1. Function - Ultra-thin glass ribbon serves as the dielectric material in glass encapsulated capacitors. The ribbon is alternately stacked with high-purity aluminum foil (unetched and unformed). Leads are attached and a glass cover is placed into position. Annealing bonds the glass ribbons and foil strips to form the body of the capacitor.

2. Input Materials - Glass ribbon and high-purity aluminum foil are the base materials for these capacitors. Lead wires are made of copper. The composition of the glass ribbon and covers is not known.

3. Operating Conditions - The assembly of glass encapsulated capacitors is performed at ambient conditions. The annealing temperature is not reported.

4. Utilities - Electricity is used to operate the assembly equipment. The annealing furance is heated with electricity or gas.

5. Waste Streams - This is a dry operation, and there are no air, water, or solid wastes known to be generated.

6. Control Technology - The use of controls for this process is not discussed in the literature.

Terminal Cleaning

1. Function - Annealing at high temperatures results in a coating of the copper leads with copper oxide. To remove the oxide, the leads are dipped into a mild sulfuric acid solution and rinsed.

2. Input Materials - Sulfuric acid and water are the input materials.

3. Operating Conditions - Terminal cleaning is presumably conducted at ambient conditions.

4. Utilities - There are no special utility requirements.

5. Waste Streams - There are no air emissions associated with this process.

A wastewater discharge results from contact cooling acid bath dumps and subsequent water rinsing. The total discharge is a function of the number of leads cleaned, rather than surface area. However, it can be related to the total number of capacitors produced because there is not a large difference in surface area between the smallest and the largest glass encapsulated capacitors. The process has been characterized by a flow of 76 to 114 liter/h and fluctuating concentration levels.[1]

There are no solid waste streams.

6. Control Technology - No special systems are used to treat the water discharge from this process. Wastewater is discharged directly to municipal treatment works.

Glass Cutting

1. Function - In a final step, special cutting disks are hydraulically lowered through a bar of uncut capacitors which have been fabricated as a group. Water sprayed over the bar and spinning disk cools the disk and flushes away sawed glass particles (kerf). The capacitors are then penetrant inspected, rinsed, electrically evaluated, and shipped.

2. Input Materials - Water is the only input material associated with this operation.

3. Operating Conditions - Glass cutting operations are presumably performed at ambient conditions.

4. Utilities - Electricity is used to operate the hydraulic cutting equipment. Water is used to cool the glass capacitor bar during cutting and to flush away glass particles.

5. Waste Streams - There are no air emissions associated with this process.

A wastewater discharge results from the water spray used to cool the bar while cutting. Total discharge is related to the cross-sectional surface area and the number of cuts. One production facility had a flow rate of 679 liter/h and high solids content in this raw wastewater stream.[1]

An additional wastewater discharge results from the wash and rinse steps of the penetrant inspection process, during which parts are examined for minute cracks and flaws. The chemical composition of the fluorescent penetrating solution is not available. This process, in which the component is dipped into a solution, examined under UV light, then washed, rinsed, and dried is not unique to the electronics industry.

There are no solid wastes.

6. Control Technology - There are not thought to be special wastewater treatment systems for this process. The effluent is likely discharged to municipal treatment works.

Oxide Formation

1. Function - An oxide film must be formed on the surface of the aluminum foil. High-purity aluminum foil is first etched to increase its effective surface area. This increases the capacitance. The foil is etched by passing current through it while submerged in strong acids, a process similar to anodizing. The forming reaction itself is an additional electrochemical operation in which a direct current potential is applied between the aluminum foil roll and the steel reaction tank, which is filled with a dilute ammonium pentaborate solution. The aluminum foil is slowly unwound and passed through the solution and then rewound. This causes an aluminum oxide film of a predetermined thickness to form on the foil.

2. Input Materials - High-purity aluminum foil is the base material. Sulfuric or nitric acids are used in the etching process. Ammonium pentaborate and water are the only other known inputs.

3. Operating Conditions - Operating conditions for the oxide formation process are presumably ambient pressure and temperature.

4. Utilities - Electricity is consumed in the electrochemical treatment of the aluminum foil. Water is used in the etching and ammonium pentaborate solutions.

5. Waste Streams - There are no air emissions from this process.

The number of water discharging operations varies from plant to plant because not all processes are used an equal number of times at each facility. Some facilities do not use the etching step. The process flow rate from the acid etch is estimated to be 300 liter/h at one plant and is characterized by batch dumps of high concentrations of acid containing dissolved metals.[1] The discharge rate from the ammonium pentaborate reaction is estimated to be 190 liter/h at one plant and is characterized by a mildly acidic solution with variable solids contents and water from subsequent rinsing.[1]

There are no solid wastes from this process.

6. Control Technology - Wastewater controls at a representative number of production facilities have not been described. One facility discharges one of its process lines directly to a municipal treatment system and the other to a sand filter which discharges to a drainage ditch.[1]

Assembly

1. Function - The etched and formed aluminum foil is cut and leads are attached. The foil is interwoven with a kraft paper spacer, wound, and inserted into a metal container. The capacitors are then placed under heavy vacuum and heated. The vacuum is released and the chamber is filled with an electrolyte which fills the capacitors. The chamber is drained, opened, and the fill holes in the capacitors are soldered closed. The capacitors are electrically aged by application of direct current. This heals voids in the oxide coating and brings the capacitance to an equilibrium value. The finished capacitors are electrically evaluated and shipped.

2. Input Materials - Lead wires, kraft paper, and a metal container are used in the assembly of these capacitors. Leads are usually made of copper, while containers can be steel or aluminum. The electrolyte is composed of water, trace amounts of ethylene glycol, phosphoric acid and/or ammonium borate. Specific quantities are not available.

3. Operating Conditions - Capacitors are placed under heavy vacuum and heated during this process. The pressure and temperature are not reported. Other assembly operations are presumably conducted at ambient conditions.

4. Utilities - Electricity is used for soldering, vacuum pumps, furnaces, and aging and testing equipment.

5. Waste Streams - The only possible source of air emissions is soldering, but emission data are not available.

There are no liquid or solid wastes reported.

6. Control Technology - The extent of engineering controls for these processes is unknown.

Dielectric Fabrication

1. Function - Mica is the dielectric material used in this type of capacitor. Pure mica is subjected to high-velocity water jets which shred it into thin, small flakes. The flakes are passed over a moving vacuum belt which dries the mica flakes and forms them into a fragile mica sheet. The mica sheet is treated with silicone resins to add strength.

2. Input Materials - Mica, water, and silicone resins are the inputs for this process. Specific quantities for these materials are not available.

3. Operating Conditions - Except for the vacuum drying step, these operations are presumably performed under ambient conditions of temperature and pressure.

4. Utilities - Water is used to shred the mica into thin, small particles. Electricity is used to operate the fabrication equipment (water pumps, conveyor belts, vacuum pumps).

5. Waste Streams - There are no air emissions associated with this process.

The process has a wastewater discharge from the water used as a medium to carry the mica flakes to the paper making process. The quantity of water discharged from a typical dielectric fabrication process is not known. The wastewater probably contains mica particles.

There are no solid wastes.

6. Control Technology - Mica particles in the wastewater are probably removed by settling and/or sand filtration before discharging to a municipal treatment works. Specific treatment systems used by industry are not described.

Ball Milling

1. Function - Ball milling is the initial step in the production of the solid ceramic substrates which are used as dielectrics in ceramic capacitors. Ceramic powders are carefully weighed and introduced into a ball mill which breaks the powders down into smaller particles. Water and occasionally a solvent are added to control the viscosity of the resulting slurry.

2. Input Materials - The ceramic substrate consists of barium titanate with trace amounts of other compounds. These powders are either purchased from vendors or manufactured at the capacitor facility. The only other inputs are organic solvents. Neither the trace constituents of the ceramic substrate nor the solvents used in the slurry are characterized in the literature, probably because of proprietary considerations.

3. Operating Conditions - Ball milling is performed under ambient conditions.

4. Utilities - Electricity is used to operate the ball mill and slurry mixers. Incoming municipal water is used for ball milling, washdown of the ball mill, and mixing.

5. Waste Streams - There are no air emissions reported for this process.

Ceramic capacitor manufacturing requires regular (usually daily) cleanout of the ball mill. The procedure requires that an operator hose down the interior of the ball mill and the surrounding area. The wastewater discharge rate varies widely according to the size of the ball mill and operator variability in cleaning. However, this does not affect the pollutant discharge mass associated with washdowns. One estimated flow rate for the ball mill washdown is 1130 liter/h.[1]

There are no solid wastes from this process.

6. Control Technology - Wastewater from this process is treated in settling tanks and/or sand filtration systems and discharged to a municipal treatment plant.

Ceramic Formation

1. Function - In this process the ceramic slurry from the ball mill is mixed with organic binders similar to those used in latex paint. The resulting slurry is sheet cast onto a moving, heated paper belt. At the end of the heated chamber, the ceramic substrate is separated from the paper belt and rolled. The resulting solid material is used as the substrate in ceramic capacitors.

2. Input Materials - Organic binders are added to the ceramic slurry to provide adhesive properties that will facilitate casting into a sheet. The specific composition of these organic binders is not available.

3. Operating Conditions - The slurry is sheet cast in a heated chamber; the operating temperature is not reported. Conditions for other process steps are assumed to be ambient.

4. Utilities - Electricity is used to operate the mixers, conveyors, and process equipment. The method of heating the curing chamber is not reported.

5. Waste Streams - There are no air emissions reported for this process. However, it is possible that organic vapors could be emitted while the mixture cures in the heated chamber.

There are no liquid or solid waste streams reported for this process.

6. Control Technology - No controls are known to be applied to this process.

Baking/Printing

1. Function - Following the formation of the ceramic sheet, the processing sequence depends on whether or not the capacitor to be manufactured is single- or multiple-layered. If single-layered, the sheet is cut into squares, cured by baking, and followed by a silver coating on both sides of each square. If multiple-layered, the ceramic sheets are first printed with a precious metal ink, then stacked in layers, followed by a heat treatment under vacuum. This latter treatment removes air voids between the sheets and hardens the ceramic so it can be cut. The layered sheets are next cut into individual capacitors and baked at high temperatures to fully cure the ceramic. Both sides of each capacitor are then coated with the conductive silver.

2. Input Materials - The major input to this process is the precious metal ink used to coat both sides of the ceramic sheets. The ink is produced by dissolving ingots of precious metal (usually silver) into solution. Further specifics are not reported.

3. Operating Conditions - The specific temperatures and pressures developed during the baking process are not reported in the literature.

4. Utilities - Electrical service will be required to operate portions of this process. The type and quantity of additional utility service is unknown.

5. Waste Streams - No air emissions associated with this process could be identified in the literature. Depending on the composition of the inks and coatings used, however, organic vapor (VOC) emissions could result.

There is no wastewater discharge associated with baking processes that do not provide their own ink. Some plants do manufacture this ink, however, and the chemical characteristics of process wastewater from a facility performing this operation are given in Table 3-6.[1]

6. Control Technology - Process wastewater discharge from a facility involved in ink manufacturing operations at a minimum is treated through a process of pH adjustment and sedimentation. Additional treatment that can be performed includes sludge dewatering and filtration of the sedimentation process effluent.

TABLE 3-6. ANALYSIS OF PROCESS WASTEWATER FROM A CERAMIC CAPACITOR INK MANUFACTURING OPERATION[1]

	mg/liter	kg/day
Toxic organics		
Benzene		
Chloroform	< 0.010[a]	
1,2 Transdichloroethylene		
Ethylbenzene	< 0.010	
Fluoranthene		
Methylene chloride	< 0.010[a]	
Napthalene		
Phenol	< 0.01	
Bis(2-ethylhexyl)phthalate	< 0.010	
Di-B-Butyl phthalate	< 0.010	
Chrysene		
Pyrene		
Toluene	< 0.010[a]	
Trichloroethylene	0.027[a]	0.0012
Total toxic organics	0.027	0.0012
Toxic metals		
Antimony	< 0.005	
Arsenic	< 0.003	
Beryllium	< 0.001	
Cadmium	0.006	0.00026
Chromium	0.061	0.00263
Copper	0.389	0.01678
Lead	0.213	0.00919
Mercury	< 0.001	
Nickel	0.056	0.00242
Selenium	< 0.003	
Silver	0.034	0.00147
Thallium	< 0.025	
Zinc	0.269	0.0116
Total toxic metals	1.028	0.0444
Non-toxic metals		
Aluminum	0.903	0.0389
Barium	3.025	0.1305
Boron	0.800	0.0345

(continued)

TABLE 3-6 (continued)

	mg/liter	kg/day
Non-toxic metals (continued)		
Calcium[b]	11.767	0.5075
Cobalt	0.005	0.00022
Iron	1.513	0.06525
Magnesium[b]	3.311	0.1428
Manganese	0.031	0.00134
Molybdenum	0.004	0.00017
Sodium[a]	370.64	15.985
Tin	0.044	0.0019
Titanium	2.770	0.1195
Vanadium	0.035	0.00151
Yttrium	< 0.001	
Total non-toxic metals	9.130	0.3938
pH	8.9	
Temperature, °C	23	
Cyanide, total		
Oil and grease		
Total organic carbon	56.0	2.415
Biological oxygen demand	38.0	1.639
Total suspended solids	56.0	2.415
Phenols		
Fluoride		

[a] Concentration found in blank sample.

[b] Metals not included in totals.

Assembly

1. Function - During final assembly, the leads are soldered to the ceramic substrate, and the capacitor is dipped in molten epoxy, or as is the case with multiple-layered capacitors, epoxy molded. The epoxy is air dried, and the capacitor is electrically evaluated and shipped.

2. Input Materials - Copper is most commonly used for capacitor leads. The epoxy materials used to encapsulate the ceramic components are not identified in the literature. The solution used to clean the leads is a mild detergent dissolved in water.

3. Operating Conditions - The exact temperatures and pressures encountered during the assembly process are not reported.

4. Utilities - The types and quantities of utility service required for this process are not reported.

5. Waste streams - There are no air emissions reported for this process.

The capacitor lead cleaning operation will produce some discharge level of wastewater; the specific composition and quantity of this waste are unknown.

There are no solid wastes associated with final assembly.

6. Control Technology - The type of system used for wastewater treatment is unknown. It is assumed that this stream is subjected to pH control and settling before discharge to the environment.

REFERENCES FOR SECTION 3

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3. Spotlight on Capacitors. Electronic News Suppl., August 18, 1980.

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SECTION 4

RESISTORS

INDUSTRY DESCRIPTION

Electronic resistors are devices that provide electrical resistance and are used in circuits for protection or current control. Resistors, like capacitors, can be divided into two broad categories, fixed and variable.

A fixed resistor has two terminals and provides relatively constant electrical resistance. The three basic types are carbon composition, wire-wound, and film. In carbon composition resistors, the element is composed of finely ground carbon or graphite, an inert nonconducting filler (usually silica), and a synthetic resin binder. The proportions of carbon and filler are adjusted to produce different resistances. Wire-wound resistors generally consist of a single layer of high resistance wire wrapped around an insulating core of ceramic or fiberglass. The element in film resistors consists of a thin layer of resistive material applied to the surface of a ceramic or glass rod or tube. Application of the film may be by spraying, dipping, evaporation, sputtering, or pyrolytic cracking of gas, depending on the material. Both carbon and metal films are used, but specific materials and manufacturing processes vary widely. Metal film resistors can provide very high resistance paths, are very accurate, and have a low temperature coefficient. They are often used when a high degree of reliability and stability is required.

Variable resistors include potentiometers and trimmers. Potentiometers have three terminals: two fixed terminals attached to each end of the resistive element, and a third attached to a tap or contact that can be moved along the element to vary the resistance. Potentiometers are usually used to control or vary voltage across a circuit branch.[1] On trimmers or rheostats two terminals are used: one stationary, and one moving. Rheostats are used primarily to limit current flowing in circuit branches.[1] Potentiometers are designed for frequent or continuous tap movement, whereas trimmers are intended for only occasional movement of the tap.

Variable resistors are manufactured with a variety of materials and processes. Potentiometers or rheostats may be wire-wound or non-wire-wound. Wire-wound potentiometers are fabricated by space-winding (i.e., winding with a specified distance between each turn of the wire) a single layer of bare resistance wire around an insulating core. Element resistance is controlled by varying the core cross section and wire diameters. Non-wire-wound potentiometers include carbon composition, conductive plastic, and cermet types. Carbon composition resistive elements can be either coated films or molded into a cavity in a plastic base. Conductive plastic elements are produced by a number of molding techniques. Cermet potentiometers are made with resistive elements composed of a ceramic and metal. Although very resistant to humidity and temperature, the abrasiveness of cermet materials may result in shorter service. Trimmer elements may be carbon composition, wire-wound, or cermet.[2]

Raw Materials

The raw materials for resistors are divided into resistive elements, contacts, encapsulants, insulators and substrates, and leads:[2,3]

- Resistive elements - Wire-wound resistors are manufactured with various wire alloys. The primary element material for carbon composition resistors (both fixed and variable) is carbon or graphite. A filler, usually silica, and a synthetic resin binder complete the mixture. Metal film resistor elements may be composed of various metals, metal alloys, or metal oxides. The most commonly used are a nickel-chromium alloy composed of the alloy with traces of other metals; tin-oxide doped with antimony; and cermet, a mix of glass and metal alloys.

  The specific composition of the carbon-resin mixture used in fabrication of conductive plastic potentiometers is not known. In addition, no information was found on the composition of materials used in cermet potentiometers and fixed resistors. Most are likely proprietary.

- Insulators/Substrates - A number of insulators or substrates are used in variable and fixed resistors. The most common types are glass, ceramic (alumina), fiberglass, flexible polyester, and various plastics.

- Contacts - Contacts, which are found only on variable resistors, may be made of brass or phosphor bronze.

- Leads - Leads are usually copper or aluminum.

- Encapsulants - A wide variety of encapsulants are used for mechanical and environmental protection of resistors. Coatings include phenolic compounds, ceramic, vitreous enamel, silicone ceramic, silicone, glass, varnish, and metal, as well as various other proprietary materials.

Products

The Bureau of the Census classifies all types of electronic resistors into SIC 3676. In 1979, domestic manufacturers sold almost 10 billion units of fixed resistors at a total market value of over $350 million. An industry breakdown of each of the major types consumed in 1977, 1978, and 1979 is presented in Figure 4-1.[4] Table 4-1 presents data on sales of the various types of resistors in the U.S. market by both domestic and foreign manufacturers in 1978 and 1979, and estimated sales for 1980 and 1983.[5,6] The total market for fixed resistors increased by almost 20 percent in 1979. Resistor-capacitor networks led with a 36 percent increase, followed by metal film resistors (28 percent), carbon films (19 percent), wire-wounds (6 percent), and carbon compositions (3 percent).[4]

It is the general consensus within the industry that growth (in numbers of units and in dollars of sales) increases in 1980 will fall short of those in 1979, partly due to the economic recession. A softening of demand for video and electronic games, as well as the automotive market, are partially responsible for the expected decline. The industrial market, which includes computers, communications, and instrumentation, also showed a slowing trend in the second quarter of 1980. However, companies heavily involved in industrial and military markets remain optimistic.[4]

As to specific resistor types, a slowdown has been expected in the carbon composition business for several years. However, it still retains a respectable share of the total resistor market, and should not disappear rapidly. On the other hand, the resistor-capacitor network market is expected to rise sharply in the next 2 to 3 years, possibly even doubling by 1982 and doubling again by 1984.

The production of wire-wound resistors remained relatively unchanged in numbers of units produced from 1978 to 1979. Rapid growth is not expected, with rates of 5 to 6 percent predicted. These resistors primarily serve the power and precision markets. The power segment is the faster growing of the two, which is due in large part to the more widespread use of metal film resistors in the

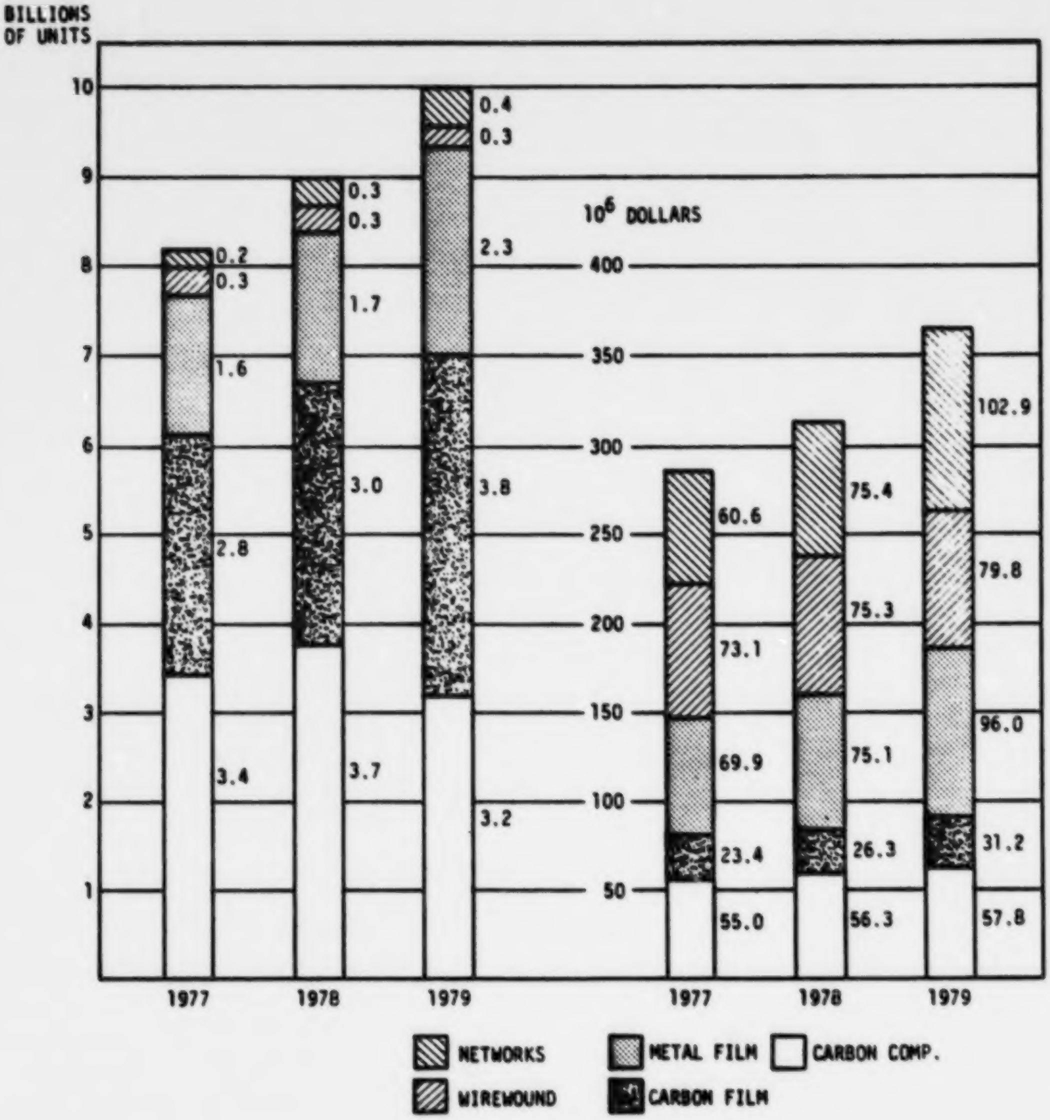

Figure 4-1. Sales of major resistor types, 1977-1979.[4]

TABLE 4-1. INDUSTRY-WIDE CONSUMPTION OF RESISTORS SHIPPED BY U.S. AND FOREIGN MANUFACTURERS FOR THE U.S. MARKET,[5,6] $ million

Resistor type	1978	1979	1980	1983	Annual growth, %
Fixed (total)	218.5	229.4	229.1	258	3.0
Carbon composition	60.0	62.3	62.6	63	0.3
Deposited carbon	21.5	23.1	22.0	26	3.0
Metal-film	75.0	79.0	81.0	99	5.8
Wire-wound	62.0	65.0	63.5	70	1.9
Variable (total)	239.5	267.2	272.0	318	4.4
Potentiometers, wire-wound	38.5	43.0	43.0	50	3.8
Potentiometers, nonwire-wound	98.5	109.7	109.0	130	4.3
Trimmers, wire-wound	22.5	24.5	25.5	28	3.4
Trimmers, nonwire-wound	80.0	90.0	94.5	110	5.1
Resistive networks (total)	149.0	177.6	198.2	269	10.9
Thin-film	69.0	79.0	88.0	114	9.6
Thick-film	80.0	98.6	110.2	155	12.0

precision area. Reluctance to redesign military circuits and lack of sufficient power ratings for metal film resistors in the power market has resulted in wire-wound resistors maintaining these areas.[4]

The market share for metal film resistors will continue to increase as their characteristics are improved. Corning, the largest producer, increased its metal film capacity by about 60 percent between the beginning of 1979 and mid-1980. Another producer, TRW-IRC, finished construction of the last of three plants in Barbados, increasing its low-cost metal film resistor output by 400 percent.[4]

Companies

The 1977 Census of Manufactures reports that a total of 102 companies are involved in the production of electronic resistors.[7] This figure excludes companies with 20 employees or less. A breakdown of companies manufacturing each type of resistor is presented in Table 4-2, and Table 4-3 categorizes these firms by number of employees.[7] Tables 4-4 and 4-5 show the product mix of the major manufacturers of fixed and variable resistors, respectively.[2] Relative market shares of the major suppliers of fixed resistors are shown in Table 4-6.[3] It can be seen that several companies manufacture more than one type of resistor, but no single company really dominates the market for more than one type.

Environmental Impacts

The manufacture of electronic resistors involves a variety of operations. Emissions of particulate matter can result from milling and trimming of metal and plastic compounds, and aerosols of silicone- or epoxy-based coatings may be released during their application. Other possible sources of atmospheric emissions are degreasing and plating tanks, and fumes and organic vapors are generated during brazing, soldering, and plastic melting processes. The principal waterborne effluents are spent solvents and other degreasing, cleaning, and cooling solutions. Scrap metals and plastics are also generated during some processes.

The types and extent of control technologies employed at resistor production facilities are not well documented in the literature. Some materials are likely recycled to the process or sold for recovery. Control of particulate

TABLE 4-2. NUMBER OF COMPANIES PRODUCING EACH RESISTOR TYPE[7]

Resistor type	Number of companies
Fixed, composition	12
Fixed, deposited carbon	17
Fixed, evaporated metal film and other metal oxide, metal/glass, or metal/ceramic element	32
Variable nonwire-wound:	
Single turn, carbon and other file, nonprecision	9
Single turn, precision and nonprecision	17
Trimmers (industrial and military grade):	
Square and round	10
Rectangular	7
Fixed, wire-wound:	
Nonprecision (fixed and adjustable) over 1%	14
Precision, unsealed	6
Precision, encapsulated and miniature, 3% or under	18
Variable, wire-wound:	
Nonprecision, single turn (wiper or shaft traverses 360° or less)	11
Precision single turn, linear (0.5% linearity or less) and and nonlinear (1% linearity or less)	17
Trimmers (industrial and military grade)	9
Miscellaneous:	
Varactors	7
Thermistors, bead type, disc, rod, etc.	12
Multiturn, all types, wire-wound and non-wirewound	12
Fixed resistor networks	15

TABLE 4-3. RESISTOR MANUFACTURERS BY EMPLOYMENT RANGE CLASSIFICATION[7]

Employment range	Number of companies
1-4	9
5-9	6
10-19	6
20-49	17
50-99	16
100-249	18
250-499	15
500-999	11
1000-2499	2

TABLE 4-4. MAJOR MANUFACTURERS OF FIXED RESISTORS[2]

	Allen-Bradley	AVX-Aerovox	Carborundum	Clarostat	Corning	Dale	Mallory	Nytronics	Ohmite	Speer	Sprague	Stackpole	TRW/IRC
Carbon composition	X								X	X		X	X
Wire-wound													
Phenolic													X
Ceramic Shell									X		X		
Flameproof						X			X				X
Vitreous enamel						X			X				
Silicone ceramic						X			X				
Silicone coated								X	X				X
Aluminum heat-sinked						X		X					
High power		X		X		X	X		X		X		X
Carbon film						X			X				X
Metal film					X	X					X		X
Cermet													X
High-voltage/high-resistance			X			X							X
Metal oxide film					X	X							
Metal film					X	X					X		X
Carbon film		X				X			X				X
Wire-wound						X		X	X				
Wire-wound, aluminum heat-sinked						X							X
Wire-wound, Bobbin						X							

TABLE 4-5. MAJOR MANUFACTURERS OF VARIABLE RESISTORS[2]

	Allen-Bradley	Bourns	Centralab	Clarostat	Mallory	Ohmite	Spectrol	Stackpole	TRW/IRC
General-purpose potentiometers									
Carbon composition	X			X	X	X		X	X
Wire-wound			X	X	X				X
Conductive plastic				X					
Cermet	X	X							X
Precision single-turn potentiometers									
Wire-wound				X			X		X
Conductive plastic							X		
Cermet							X		
Single-turn trimmers									
Carbon composition	X		X	X		X		X	
Wire-wound		X					X		X
Cermet	X	X	X				X		X
Rectangular multi-turn trimmers									
Carbon composition	X	X							
Wire-wound		X		X		X	X		X
Cermet	X	X				X	X		X
Square multi-turn trimmers									
Wire-wound		X					X		X
Cermet		X					X		X
Rheostats, all types					X		X		
Precision multi-turn potentiometers									
Wire-wound	X						X		X
Conductive plastic	X								

TABLE 4-6. MARKET SHARES OF MAJOR RESISTOR SUPPLIERS[3]

Type resistor	Company	Market share (%)
Wire-wound	TRW/IRC	28
	Dale	25
	RCL	12
	Ohmite	9
	Smallcross	5
	All others	21
Metal film	Corning	33
	Dale	20
	TRW/IRC	20
	Mepco/Electra	17
	All others	10
Networks	CTS	30
	Beckman	20
	Sprague	10
	Centralab	10
	Allen-Bradley	9
	Dale	9
	All others	10
Carbon film	R-Ohm	35
	Mepco/Electra	28
	KOA Speer	25
	All others	12
Carbon Compositions	Allen-Bradley	57
	Stackpole	23
	TRW-IRC	20

matter and organic vapors can be effected through use of readily available control devices. Wastewater streams can be treated by precipitation, settling, and subsequent filtration, as well as other methods.

INDUSTRY ANALYSIS

The following industry analysis considers each individual production operation (or series of closely related operations), called here a process, to examine in detail its purpose and actual or potential effect on the environment. Each process is examined in the following aspects:

1. Function
2. Input materials
3. Operating conditions
4. Utilities
5. Waste streams
6. Control technology

Figure 4-2 is a flowsheet showing the processes used for resistors, as well as their interrelationships and waste streams.

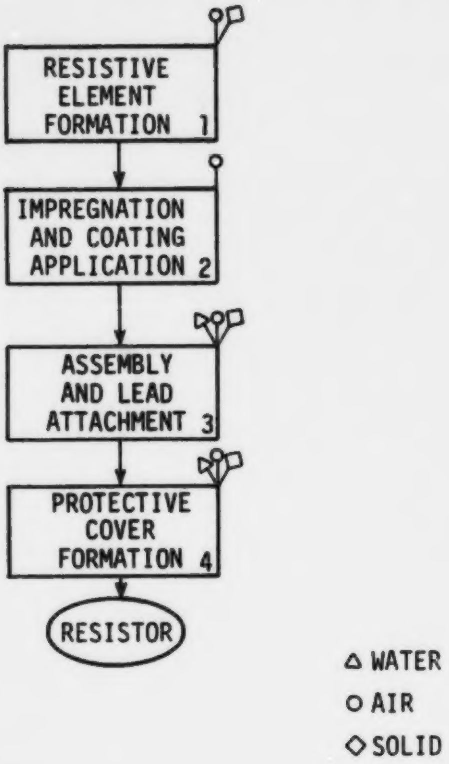
RESISTIVE ELEMENT FORMATION 1
IMPREGNATION AND COATING APPLICATION 2
ASSEMBLY AND LEAD ATTACHMENT 3
PROTECTIVE COVER FORMATION 4
RESISTOR
△ WATER
○ AIR
◇ SOLID

Figure 4-2. Resistor production flowsheet.

Resistive Element Formation

1. Function - The resistive element is the heart of the resistor. Elements can be carbon composition, conductive plastic, cermet, metal film, and wire-wound. Differing manufacturing techniques are used for each type.

The material for carbon composition resistors is carbon or graphite milled to a powder. A binder and filler is mixed with the powder and molded or extruded using either heat, pressure, or both.[2,8] Heat is applied in a baking process to remove gaseous impurities and to catalyze the binding agent; this results in adhesion of the particles into a solid mass. The cores are then formed by molding into a cylindrical shape. It is reported that in variable resistors the resistive element is molded into a plastic base to produce one integral unit. The carbon resistive element usually requires trimming, which can be performed by a mechanical etch. Methods of trimming in thick film applications include air abrasion, pulse trimming, scribe trimming, and laser trimming.[9]

Carbon film resistor elements are manufactured by application of a layer of carbon to glass, ceramic, or other insulating materials. The application methods are by screen-on through a mask, brush-on spraying, and dipping.[9] Adhesion of the film to the substrate is enhanced by baking or heating. A pyrolytic process to decompose gaseous hydrocarbons and cure the film is also reported.[8] A variation of carbon film, known as cracked-carbon film, is provided with a helical groove cut around the cylinder to allow adjustment of final resistance. This spiralling can be made with a high-velocity air stream propelling an abrasive powder, a thin high-speed grinding wheel, or a laser.[2] As the resistor is turned, the cutting tool traverses its length.

Conductive plastic resistor elements are made of a carbon-resin mix. This composition is either molded into a plastic substrate or molded simultaneously with the substrate. In the latter case, the carbon-resin mix is sprayed onto a plastic preform prior to application of heat and pressure. Conductive plastic mixes may also be applied to flexible polyester, molded plastic, or ceramic substrates by silk-screening methods.[2]

Cermet resistor films are usually mixtures of precious metals or metal oxides and glass frit. Inks made by adding an organic vehicle of suitable viscosity to the cermet powder are applied to an insulating substrate, usually by silk-screening or brushing to form the cermet film. The element is then fired to cure the cermet. A casting method in which the cermet powder is made into a slurry and cast into a continuous flexible sheet for later application has also been devised. The advantage of this method is less waste of material. Films are usually 6 to 50 μm thick.[9]

Metal film resistors are made by coating a glass or ceramic substrate with a thin film of metal by vacuum evaporation, sputtering, or chemical vapor deposition by pyrolytic decomposition of gases.[2,9] The substrate is glazed prior to metal deposition and then overglazed after deposition to protect the metal film.[9] The overglaze must be alkali-free to prevent ionic conduction and degradation. The resistor is fired after deposition.

Wire-wound resistor elements are produced by space-winding (i.e., winding the wire so that there is a specific distance between each turn) a single layer of conductive wire around an insulating core.

2. Input Materials - Primary materials used in resistive element fabrication include carbon, graphite, metals, and metal oxides.[8,9] Ceramics, plastics, resins, binders, and fillers are also employed. Carbon and graphite are the major components of carbon composition resistive elements. Fillers used in these devices include silica sand and titanium oxide.[8] One binding reported in the literature is zinc stearate.[8] Another material added is boron, which improves performance by preventing oxidation of the carbon.[9]

Carbon and resin are used for conductive plastic resistor elements. Plastics used as substrates may be thermosetting plastics (e.g., phenolics, alkyds, epoxies, diallyl phthalates, silicones) or thermoplastics (e.g., polyesters, polyimides, cellulose, polystyrene).[9] Flexible insulating substrates that might be used include cotton or glass cloth impregnated with oleoresins, phenolic resins, alkyds, epoxies, or silicones; inorganic paper insulations composed of asbestos, wood pulp, starch, or rubber binder (possibly containing glass flakes, resin binder, polyvinyl acetate, epoxy, or silicones); and 2- or 3-ply combinations of polyester, acetate, or polyimide bonded with rubber adhesive and mat film composites of polyester between 2 layers of acrylic- or polyester-based mat.[9]

Various metals and metal oxides are used as the resistive element. For wire-wound resistors, nickel-chrome wire in various combinations is most often employed. Table 4-7 lists some of these wire alloys.[2]

TABLE 4-7. CHARACTERISTICS OF ALLOYS USED IN WIRE-WOUND POTENTIOMETERS AND RESISTORS[2]

Alloy	Approximate composition
Evanohm[a]	Ni 75%, Cr 20%, Al 2.5%, Cu 2.5%
Nichrome[b]	Ni 60%, Cr 16%, Fe 24%
Advance[b]	Ni 43%, Cu 57%
Cupron[a]	Cu 55%, Ni 45%
Midohm[b]	Ni 23%, Cu 77%
No. 90 Alloy[a]	Ni 12%, Cu 88%
Lohm[b]	Ni 6%, Cu 94%
No. 30 Alloy[a]	Ni 2%, Cu 98%
Copper	Cu 100%

[a] Trademark, Wilbur B. Driver.

[b] Trademark, Driver-Harris.

Cermet films are composed of various mixtures of metal, metal oxides, and glass or ceramic. Metals usually used include silver, platinum, ruthenium oxide, irridium oxide, gold, palladium, and palladium oxide.[9] One cermet reported is a mixture of palladium, silver, and lead-borosilicate glass.[9] These are mixed in an organic vehicle for application. Specific organics were not identified in the literature.

Ceramics used as insulating elements or substrate are usually composed of alumina (Al_2O_3).

3. Operating Conditions - Heat and pressure are used to fuse and form resistive elements, or to cure and fire them after deposition on a substrate. Specific temperatures used in baking or firing are not generally reported. For drying films printed on a substrate, temperatures from 100° to 150°C for 15 minutes are required.[9] This is accomplished in a hot air or infrared moving-belt furnace. Temperatures of 450° to 1000°C are required to burn off organic binders.[9] These temperatures are also required to develop proper film parameters and to sinter the colloidal glass used in certain resistor coatings. Pressures used in forming carbon-graphite resistive cores are not reported.

4. Utilities - Electricity is required for operating various machinery used for molding, extruding, wire winding, spraying, mixing, vacuum deposition, and heating. Dryers and ovens for firing operations may be gas-fired. Water may be used in conjunction with the trimming operation to flush away the particles.

5. Waste Streams - Trimming operations could result in generation of airborne particulates. This could also be true of milling of carbon and graphite prior to molding. Airborne materials would be primarily carbon and/or graphite, as well as some silica, titanium oxide, boron, and metal oxides. Volatile organics and other impurities are emitted during drying and firing operations. Some volatile constituents of the various plastics and resins used in manufacturing of conductive plastic resistors may also be released. Other areas of potential airborne waste streams include aerosols and vapors emitted during spraying operations.

There are no sources of process wastewater described in the literature.

The only source of solid wastes would be scrap materials from trimming of carbon composition resistive elements, off-spec materials, and mask disposal from screen-on operations.

6. Control Technology - Specific control technologies used in resistor manufacture are not cited in the literature. However, removal of particulate and organic vapors would be required in some cases. Particulate removal can be accomplished using cyclone separators, baghouses, and electrostatic precipitators. Organic vapors can be removed by passing the contaminated air through an activated carbon filter.

Impregnation and Coating Application

1. Function - Impregnation is performed to waterproof the porous carbon resistor elements. Barrier coatings are applied tc wire-wound resistors. Their functions are to provide some degree of moisture, gas, and dust prevention, thus preventing corrosion and electrical malfunctions; to provide an insulation barrier; to provide stress relief during molding and thermal cycling; and to hold components together, thus increasing their ruggedness.[9]

Impregnation consists of immersing the element in the liquid material to thoroughly soak and wet any interstices present. This is usually accomplished with vacuum or pressure equipment.[9] The material is then cured with heat. Application of barrier coatings is accomplished by a number of methods; these include dipping, spraying, fluidized-bed, and eye dropping.[9] These coatings are also cured with heat following application.

2. Input Materials - Impregnants are usually various types of lacquers, varnishes, or waxes. Specific types used are generally not reported in the literature. In one plant surveyed, polychlorinated bipheynyls (PCB's) were used to impregnate resistor cores.[8] At the time of the survey, however, these operations were being phased out.

A variety of materials, usually high-molecular-weight polymers, are used for coatings. Most widely used are silicone- or epoxy-based substances.[8,9] Other coating materials may be polyester, polyvinyl formal, and polyvinyl butyral.[9]

3. Operating Conditions - Impregnation is accomplished in pressure or vacuum cycling apparatus. Specific pressures or vacuum settings are not cited in the available literature. Curing temperatures required will vary with the impregnate or coating. For various silicone coatings, cure temperatures range from 60°C for 4 hours to 250°C for 4 hours.[9]

4. Utilities - Electricity is required for operation of various types of machinery performing operations such as molding, injection, extrusion, spraying, eye dropping, and fluidized-bed. Compressed air may be required for pressure application machines, and some ovens are gas-fired. Water is likely required in some applications.

5. Waste Streams - Airborne waste streams would be primarily from loss of materials during application processes. Aerosols and high vapor pressure constituents would be emitted, especially during such application processes as spraying and fluidized-bed.

Cleaning of equipment will most likely require solvents which will require disposal. Other process liquid wastes are not reported.

There are no solid wastes from this process.

6. Control Technology - Control of organic vapors could be accomplished by collecting vapors via hoods and passing them through an activated carbon bed.

Any waste solvents generated by cleaning could be reclaimed by the manufacturer or sent for reclamation or disposal. Information on specific treatment methodologies presently in use at manufacturing plants is not available.

Assembly and Lead Attachment

1. Function - Final assembly and lead attachment varies with resistor type. In molded carbon composition resistors, leads may be embedded in the resistive core at the time it is formed. They may also be welded, brazed, or soldered to an end cap that is mechanically force-fit onto the ends of the carbon composition core. In carbon film-type resistors, the leads may be inserted into the glass or ceramic rod on which the resistive coating was applied. At the ends of the tube, a connection is made between the coated glass and leads with conductive cement. In wire-wound resistors, the lead wire may be mechanically crimped to the resistance wire element. Alternatively, the resistance wire may be welded to a nickel-chrome wire which is then brazed to the inside of an end cap with an attached lead. The lead may be brazed directly to the resistance wire.[10]

Variable resistors require assembly of a larger number of component parts than do fixed resistors. The resistance track, sliding contact, spindle, bearing assembly (in some instances), and the three terminals may all require assembly. Details of assembly methods were not found in the literature.

2. Input Materials - Input materials are primarily various metal parts. Leads may be copper, silver, aluminum, gold, or wire plated with tin, silver, or gold. A variety of alloys may be made with these metals using nickel, chromium, palladium, iron, molybdenum, tungsten, and magnesium. Sliding contacts on variable resistors may be brass, bronze, or phosphoric bronze.[2,8] A copper-graphite contact has also been reported.[10] One conductive cement reported to be used in electronic component assembly is a silver-based epoxy.[8] The most commonly used solder in the resistor industry is 60/40 tin/lead alloy.[8] Various acid fluxes containing zinc chloride, ammonium chloride, hydrochloric acid, or stannous chloride may be used in soldering operations. Brazing filler metals may include copper, copper-phosphorus, aluminum-silicon, and silver-, gold-, and nickel-based alloys. Fluxes or resin co-solders may also be used in brazing operations.

3. Operating Conditions - Mechanical lead attachment and various assembly operations are performed at ambient temperature and pressure. Soldering operations involve melting temperatures below 500°C, whereas brazing involves higher temperatures. Other wire assembly methods may include thermal compression and ultrasonic bonding. Temperatures and pressures used in thermal compression bonding would depend on the metal or alloy.

4. Utilities - Electricity would be required for operation of machinery for assembly, soldering, welding, or brazing operations. Process water may be required for cooling and cleaning purposes.

5. Waste Streams - The only air emissions are fumes from brazing and soldering operations.

Removal of solder flux could possibly result in small amounts of contaminated water containing metals.

Solder dross and scrap metal from brazing, soldering, wire forming, and cutoff operations represent potential solid wastes from lead attachment and assembly operations.[8]

6. Control Technology - Fumes from soldering and/or brazing operations will require collection and treatment. Satisfactory treatment could be accomplished using a packed tower scrubber.

Wastewater containing acid flux and metal wastes can be treated by pH adjustment to neutralize the waste and precipitate the metals. Subsequent filtration may or may not be required. Sludge can be disposed of in a secured landfill or, if feasible, sold for recovery.

Most metals in the form of scrap will likely be recovered and sold for reprocessing, especially precious metal scrap.

Protective Cover Formation

1. Function - The purposes of a final cover for resistors (as well as other electronic components) are to provide a well-defined structure to permit standardization and interchangeability of parts; to provide a degree of impact and mechanical shock resistance; and to provide some degree of environmental protection from moisture, sunlight, and various corrosive agents.[9] Final covers for resistors are either metal, a combination of a thermosetting or thermoplastics and metal, or thermosetting or thermoplastics alone.

The processes used for embedding, which is employed primarily for plastic materials, can be categorized generally into four types: casting, potting, encapsulation, and transfer molding. Casting consists of pouring a catalyzed thermosetting plastic or a thermoplastic liquid into a reusable mold. Potting is basically the same as casting, with the major exception that the mold (metal or plastic) becomes an integral part of the component. Encapsulation coating is usually by dipping into a curable or hardenable plastic. These coatings are relatively thick compared to barrier coatings. Encapsulation can also be accomplished using spray techniques. Transfer molding involves the transfer of a catalyzed or hardenable material under pressure from a container into a mold which contains the part to be covered.[9]

Some resistors may be hermetically sealed in small metal cannisters or, as is the case many times with variable resistors, sealed in molded plastic or plastic/metal cases. Metal cases usually require cleaning and subsequent plating.

2. Input Materials - A variety of materials can be used for protective coverings. Metals are usually steel, aluminum, and brass, which are often tin- or nickel-plated.

Thermosetting plastics (which cure chemically) used for embedding include alkyds, aminos, diallyl pthalates, epoxies, phenolics, polyesters, and silicones. Embedding thermoplastics (which liquify under heat and pressure and harden when cool) include ABS (acrylonitrile, butadiene, and styrene), acetals, acrylics, ethylene vinyl acetates (EVA), fluorocarbons, nylons, phenoxies, polyimides, polycarbonates, polyesters, and polystyrenes.[9]

Degreasing of metal used for covers may involve use of various halogenated and non-halogenated solvents. Most commonly used halogenated solvents are perchloroethylene and 1,1,1 trichloroethane. Non-halogenated solvents include methanol, acetone, Stoddard solvent, methyl ethyl ketone (MEK), and isopropyl alcohol.[8]

Plating of metal cans involves use of nickel and tin plating solutions. The composition of typical solutions can be found in the discussion of printed circuit board manufacture in Section 6.

3. Operating Conditions - Operating conditions of temperature and pressure vary widely depending on specific materials and processes used.

4. Utilities - Electricity would be required to run various machines used for molding and dispensing liquid materials, and to supply heat for melting thermoplastics. Water is probably required for cooling and cleaning purposes.

5. Waste Streams - Some airborne emissions would result from encapsulation by the spray method, from degreasing tanks, plating tanks, and (depending on the material) from melting of plastics.

The only liquid wastes would be used chlorinated or petroleum-based hydrocarbon degreasing solutions from metal cleaning, wasted nickel or tin plating solutions, and other contaminated cleaning and cooling water.

Solid wastes include scrap from trimming the molded components, unused portions of mixed thermosetting plastics which cannot be reused, off-spec plastics, and metal scrap.

6. Control Technology - Emissions from degreasing tanks can be reduced by increasing freeboard in the degreaser tank and using refrigerated chillers to create a cold air blanket above the solvent. Emissions can be controlled by the use of chillers or condensers and carbon adsorption.[11] Spraying emissions can be reduced by use of water curtains or dry baffles.[12]

Rinse water and dumped plating solutions will contain tin and nickel and can be treated by pH adjustment using lime, precipitation, settling, and subsequent filtration of supernatant using diatomaceous earth. Other techniques used for recovery of plating solutions include reverse osmosis, distillation, and ion exchange. Sludges from treatment of plating solutions can be dewatered by centrifuge, vacuum filter, or pressure filter apparatus, and disposed of by landfilling.[13,14] Non-halogenated hydrocarbons used for cleaning, such as methanol, acetone, MEK, and ispropyl alcohol, are usually reclaimed on-site or sent away for recycle.[8] Halogenated solvents such as perchloroethylene and 1,1,1 trichloroethane are again either reclaimed on-site or given to a contractor for reclamation.[8]

Waste thermoplastic materials may be recycled through the molding process, since they can usually be melted and remelted.[8] They may also be hauled to a landfill along with thermosetting plastic wastes.[8] Metal scrap can be recovered and recycled where feasible. Bottoms from degreasing tanks may warrant reclamation if metals content is high, but are usually drummed and landfilled.

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SECTION 5

TRANSFORMERS AND INDUCTORS

INDUSTRY DESCRIPTION

An electronic transformer is used to convert variations of AC current in a primary circuit into variations of voltage and current in a secondary circuit through mutual induction. A transformer is basically two coils of wire in close proximity on a common core; if one coil is energized, a magnetic field is created which, depending on its strength or polarity, induces the flow of a secondary current in the other coil. If an AC voltage is applied to one coil, an AC voltage of the same frequency is induced in the other coil. The magnitude of this induced voltage is approximately equal to the applied voltage times the ratio of the number of turns on each coil. The degree of induction is dependent to a large extent on the nature and construction of the core.[1]

Transformers are made in great variety, many times to meet a specific application requirement. Four basic types of transformers are power, audio, pulse, and radio frequency (rf). Power transformers change an AC power supply voltage and current to that required for operation of electronic equipment. Audio and communications transformers transmit information of varying frequency, amplitude, and wave shape between electronic equipment or between circuits in a single piece of equipment. They are used to couple signals whose frequencies fall in the 20 to 20,000 Hz range. Pulse transformers operate over a wide band of frequencies and are designed to transmit pulses with good waveshape fidelity, rather than the continuous sinusoidal wave resulting with audio transformers.[1] Radio-frequency transformers are used to couple high-frequency signals and thus the cores are composed of powdered iron or ferrite to minimize energy losses. These type cores are used up to about 50 MHz. Above this frequency air cores are often used.[10]

Closely related to a transformer is an induction coil, or inductor, which is basically a single wire wound around an air or magnetic core with a terminal at each end of the winding. The inductance of this wire coil is a measure of its ability to induce a current to flow when subjected to a magnetic field or, conversely, the ability to produce a magnetic field when current is passed through the coil. The magnetic field produced stores energy, the amount depending on the magnitude of the current. When the current flowing in an inductor reaches a steady value, the magnetic field also stabilizes and stores a steady value of energy. The energy stored increases as the square of the magnitude of the current. The magnitude of the inductance of a coil is determined by the number of coil turns, the type and shape of the core material, and the diameter and spacing of the turns. Inductors may be used as power supply filters, oscillators, frequency discriminating filters, and for tuning circuits.[1]

Inductor design is essentially dependent upon operating frequency. Magnetic cores are used at audio and low carrier frequencies to combine large inductance and low DC resistance. In low frequency applications a high inductance value is required, the core material must have a high permeability, and the number of coil turns must be large. The laminated cores used for these applications are made of thin sheets of steel or other iron alloys separated by insulating glue. These laminated cores can be used since at low frequencies, energy losses due to eddy currents and hysteresis are small. In applications where core losses need to be minimized such as in high-frequency inductors, ferrites, powdered iron, or other high permeability magnetic alloys can be used.[1,10]

Raw Materials

Raw materials can be broken down into core materials, windings, and encapsulants:[1,2]

- Core materials - Core materials are usually composed of iron, an iron alloy, or a ferrite. A current flowing through a primary winding may induce current flow through the magnetic core as well as the secondary winding. The usefulness of a solid iron block as the core is therefore limited, as the current flow in the magnetic core or eddy current creates its own magnetic field which opposes the field induced by the primary winding and results in power losses. To alleviate this problem, cores are made by stacking thin sheets of metal with an insulating glue between each. This serves to break up the electrical continuity of the cores. Some cores are made by compressing grains of ferrous metal together with an insulating binder. Ferrites or artificial magnets, composed chiefly of iron oxide and other metallic ions, are preferred for high-frequency and audio applications because of their high permeability and inherent electrical resistance. Soft ferrites are also used in some transformer cores. These are usually made from combinations of nickel, zinc, and iron oxides; manganese, zinc, and iron oxides; and nickel, copper, zinc, and iron oxides. Inductor cores are also made of iron, iron alloys, and ferrites. Phenolic compounds, air, and air and phenolic combinations are also used. Table 5-1 lists some high permeability magnetic materials and alloys, many of which are used in coils and transformers.[3]

- Coil materials - Very little information is available in the literature concerning specific winding materials. Copper and aluminum wire are probably the most widely used windings. Lesser amounts of other conductive metals such as silver, gold, nickel, and chromium may also be used to increase conductivity. In some applications, metal pastes with a conductive metal covering are employed.

- Encapsulants - In the manufacture of laminated cores, varnish, lacquer, or wax generally serve as an impregnant to prevent any vibration of the laminations. These materials may also be used in transformers with other core types to prevent vibration of the winding. In some cases, the assembly itself may be encapsulated with an epoxy molding, resin, or metal case.

Products

The Bureau of the Census classifies the manufacture of electronic transformers, coils, and inductors into SIC 3677. This SIC classification does not include the following related products:

- Transformers and inductors for telephone and telegraph apparatus (SIC 3661)
- Electric lamps (SIC 3641)
- Coils for electrical end uses in industry (SIC 3629)
- Electrical transformers (SIC 3612)
- Semiconductor (solid state) and related devices (SIC 3674)

a breakdown of the various components produced under this SIC in 1977 is presented in Table 5-2.[4]

It is reported that the total value of shipments increased 43 percent from 1972 to 1977.[4] As can be seen in Table 5-3, this growth rate is expected to decrease significantly.[5,6] An annual growth rate of only 4.2 percent is estimated from 1978 to 1983.

TABLE 5-1. HIGH PERMEABILITY MATERIALS AND ALLOYS[3]

Material	Form	Approximate percent composition					Use
		Fe	Ni	Co	Mo	Other	
Cold rolled steel	Sheet	98.5					
Iron	Sheet	99.91					
Purified iron	Sheet	99.95					
4% silicon-iron	Sheet	96				4 Si	Low core losses
Grain oriented	Sheet	97				3 Si	
45 Permalloy	Sheet	54.7	45			0.3 Mn	Audio transformers, coils and relays
Hipernik	Sheet	50	50				
Monimax	Sheet	50	47		3		High frequency coils
Sinimax	Sheet	54	43			3 Si	High frequency coils
78 Permalloy	Sheet	21.2	78.5			0.3 Mn	
4-79 Permalloy	Sheet	16.7	79			0.3 Mn	Audio coils, transformers, magnetic shields
MuMetal	Sheet	18	75			2 Cr 5 Cu	Audio coils, magnetic shields, transformers
Supermalloy	Sheet	15.7	79			0.3 Mn	Pulse transformers, magnetic amplifiers, coils
Permendur	Sheet	49.7		50		0.3 Mn	
2V Permendur	Sheet	49		49		2 V	D-C electromagnets, pole tips
Hiperco	Sheet	64		34		Cr	

TABLE 5-2. SHIPMENTS OF ELECTRONIC TRANSFORMERS, INDUCTORS, AND COILS, 1977[4]

Component description	Product shipments	
	Quantity, million	Value, $ million
Coils, transformers, reactors, and chokes for electronic applications:		
As reported in the Census of Manufactures	NA	588.4
As reported in Current Industrial Reports MA-36N, selected electronic and associated products, including telephone and telegraph apparatus	NA	560.5
Audio transformers	26.8	63.5
Low frequency chokes	11.0	19.6
Plate and filament transformers, including autotransformers, except toroidal	33.9	152.3
Pulse transformers, computer, and other types	21.3	40.7
Radio frequency (RF) chokes	94.1	19.7
RF coils	NA	37.6
Intermediate frequency (IF) transformers	16.0	12.7
Television deflection, focus coils, deflection yokes, etc.	18.5	81.4
Toroidal windings (transformers and reactors), except complete magnetic amplifiers	33.9	52.3
Other (balum coils, permeability tuning devices, etc.)	NA	80.7
Coil, transformers, reactors, and chokes for electronic applicaton, not specified by kind, typically for establishments with less than 20 employees	NA	17.4

NA - Not available.

TABLE 5-3. MARKET ESTIMATES FOR COILS, TRANSFORMERS, AND CHOKES,[5,6]

Product	Sales, $ million				Annual growth, %
	1978	1979	1980	1983	
Total - transformers, coils and chokes	795.2	852.1	872.0	984	4.2
Transformers and chokes, except T.V.	269.0	299.0	316.0	382	7.0
Transformers and chokes, laminated	1720	193.0	205.0	237	7.1
Transformers and chokes, torroidal	57.0	62.0	65.0	80	6.3
Pulse transformers	40.0	44.0	46.0	65	7.7
Rf coils	15.8	14.7	13.0	10	-10.2
TV magnetic components	171.4	176.4	177.0	200	2.3

Companies

According to data presented in the 1977 Census of Manufactures, 294 companies were engaged in the manufacture of coils and transformers for electronic applications.[4] A breakdown of these companies is given in Table 5-4.[4] Table 5-5 shows their size by total employment.[4] A list of some major transformer and inductor manufacturers is given in Table 5-6.[1] There are three principal companies that produce a full line of iron and ferrite core transformers and inductors: Stancor, Thordarson Meissner, and TRW/UTC. Each of these companies also manufactures miniature and smaller units and, with the exception of Stancor, pulse transformers. Radio frequency inductors are produced only by other companies.

Environmental Impacts

Very few data are available in the literature concerning emissions during the manufacture of transformers and inductors. Dusts and particulate matter may result from grinding operations associated with core fabrication, and organics may be released during impregnation and curing of coatings. There is also scrap in the form of metals from core fabrication and contaminated impregnant and coating materials (plastics, resins). The use of specific control technologies or disposition of scrap materials are not reported.

INDUSTRY ANALYSIS

The following industry analysis considers each individual production operation (or series of closely related operations), called here a process, to examine in detail its purpose and actual or potential effect on the environment. Each process is examined in the following aspects:

1. Function
2. Input materials
3. Operating conditions
4. Utilities
5. Waste streams
6. Control technology

Figure 5-1 is a flowsheet of the processes used for transformers, as well as their interrelationships and waste streams.

TABLE 5-4. COMPANIES MANUFACTURING VARIOUS PRODUCTS UNDER SIC 3677[4]

Transformer type	Number of companies
Audio transformers	87
Low frequency chokes	84
Plate and filament transformers, including autotransformers, except torroidal	101
Pulse transformers, computer, and other types	59
Radio frequency (RF) chokes	37
RF coils	33
Intermediate frequency (IF) transformers	24
Television transformers and reactors (horizontal output, vertical deflection, focus coils, deflection yokes, etc.)	21
Other (balun coils, permeability tuning devices, etc.)	51

TABLE 5-5. DISTRIBUTION OF COMPANY SIZE IN SIC 3677 BY TOTAL EMPLOYMENT[4]

Employment range	Number of companies
1 to 4 employees	33
5 to 9 employees	23
10 to 19 employees	44
20 to 49 employees	69
50 to 99 employees	67
100 to 249 employees	44
250 to 499 employees	10
500 to 999 employees	3
1,000 to 2,499 employees	1
Total	294

TABLE 5-6. TRANSFORMER AND INDUCTOR MANUFACTURERS

	James Millen	J. W. Miller	Microtran	Nytronics	Pico	Sprague	Stancor	Thordarson Meissner	TRW/UTC
Iron core transformers and inductors (full line)							X	X	X
Miniature, subminiature, and ultraminiature transformers and inductors			X		X		X	X	X
Pulse transformers					X	X		X	X
Radio frequency inductors	X	X		X					

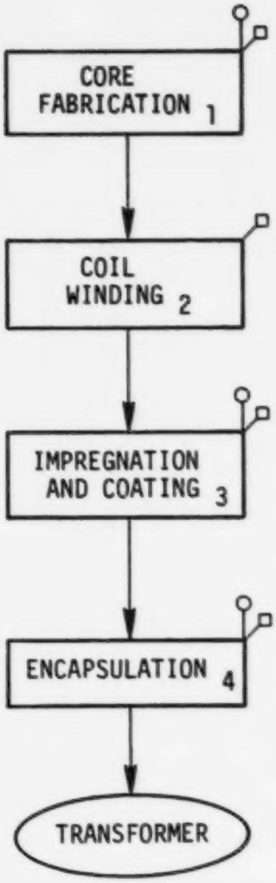
CORE FABRICATION 1
COIL WINDING 2
IMPREGNATION AND COATING 3
ENCAPSULATION 4
TRANSFORMER

Figure 5-1. Transformer production flowsheet.

Core Fabrication

1. Function - A transformer core must be fabricated with characteristics suitable for its intended application. Laminated cores are often used in low frequency (20 to 20,000 Hz) applications such as in audio-frequency transformers.[10] High-permeability magnetic alloys or ferrites are used in high-frequency applications where accurate inductance is required.

High-permeability magnetic alloys or soft magnetic alloys have low magnetic hysteresis loss resulting from variations in the magnetic flux produced within the alloy and a low residual magnetism even after being highly magnetized.[7] Alloys of nickel-iron, cobalt-iron, and silicon-iron may be used. Heat treatment must be performed to increase the high-permeability characteristics of commercially available nickel-iron alloys. These steps should be conducted in a nonoxidizing, noncarburizing, noncontaminating atmosphere.[7] Dry hydrogen is recommended as the best atmosphere, although dissociated ammonia, argon, dry nitrogen, and vacuum are also used. One recommended heat treatment process to obtain highest permeability involves heating in a sealed retort filled with a protective atmosphere for 2 to 4 hours at 1130° to 1170°C. After cooling to 200°C, an inert atmosphere is introduced until the temperature is below 100°C.[7] Various types of nickel-iron alloys may also be produced in laminations that can be stacked with insulating glue.

Silicon-iron alloys are low in cost, and though their response to magnetic fields is inferior to nickel-iron alloys, their magnetic characteristics are superior under certain conditions. Alloys in thick strip and bar forms are fabricated into many shapes of magnetic cores by machining, forging, and precision casting operations. Heat treatment is required to obtain uniform magnetic properties from part to part, and magnetic properties improve with increasing heat-treating temperature. Cobalt-iron alloys are used for their high magnetic saturation and relatively low coercive force in AC and DC applications. Commercial irons and commercially pure irons are also used for cores; they have good magnetic properties and are relatively low in cost compared to many alloys. Magnetic properties vary depending on the manufacturer and degree of heat treatment. These products are usually manufactured by consumable electrode melting or vacuum induction melting to assure low carbon content, low gas content, and a minimum of residual elements.

2. Input Materials - Raw materials for transformer and inductor cores are usually high-permeability alloys. High-permeability alloys can be subdivided into nickel-iron alloys, cobalt-iron alloys, silicon-iron alloys, and commercial and commercially pure irons.[2] Table 5-7 gives approximate compositions of some nickel-iron alloys.[7] Silicon-iron alloys contain usually 1.0 to 2.5 percent silicon with the remainder iron, though silicon content may be as high as 4 percent.[7] Some commercial silicon-iron alloys include Hipersil (4 percent Si, 96 percent Fe), and silicon core iron 1, 2.5, or 4 percent Si; balance Fe). Table 5-8 gives compositions of some cobalt-iron alloys.[7] Some commercial and commercially pure irons include ingot iron (Armco, Consumet), Vacumet core irons (Carpenter Technology), and Ferrovac E (Crucible Steel). Cores may also be fabricated using phenolic compounds, and some transformers and inductors have air cores.

3. Operating Conditions - Heat treatment is crucial in obtaining the desired characteristics for high-permeability alloys. The following conditions are recommended:[7]

Alloy	Temperature, °C	Time
Nickel-iron	1120-1170	2-4 hours
Silicon-iron	1350-1950	2 hours
Cobalt-iron	815-925	2 hours
Irons	850-1000	2 hours

4. Utilities - Electric or natural gas is required to heat furnaces for heat treatment of the varous alloys. Electricity is also required for fan motors.

5. Waste Streams - Airborne dusts could be released during grinding operations. There are no other atmospheric emissions reported.

There are no wastewater effluents from this process.

Scrap metals are generated as a result of various machining operations.

TABLE 5-7. HIGH-PERMEABILITY NICKEL-IRON ALLOYS[7]

Approximate composition	Commercial name
80% Ni, 4% Mo, balance Fe	4-7,9 Permalloy HyMu 80 Hipernon
77% Ni, 1.5% Cr, 5% Cu, balance Fe	MuMetal
49% Ni, balance Fe	Deltamax HyRa 49 High Permeability 49 Hipernik and Hipernik V Universal-Cyclops Simmonds Saw and Steel Co. Armco Steel Corp.
45% Ni, balance Fe	
49% Ni, 0.15% Se, balance Fe	
47% Ni, 3%3 Mo, balance Fe	
80% Ni, 5% Mo, balance Fe	

TABLE 5-8. COBALT-IRON ALLOYS[7]

Alloy composition	Commercial name
50% Co, 50% Fe	Permendur, Hy-Sat 50
49% Co, 49% Fe, 2% V	Hiperco 50, Hy-Sat 48, 2-Vanadium Permendur
49% Co, 49% Fe, 2% V	Hy-Sat 48 FM
35% Co, 1% Cr, balance Fe	Hiperco 27, Hy-Sat 27

6. Control Technology - Dust from grinding operations would probably be captured by exhaust hooding and routed to a cyclone separator. Dusts would be drummed and landfilled or if economical, recycled.

Most scrap metal waste would likely be recovered and sold for reclamation.

Coil Winding

1. Function - Wire must be wound around a core to form a transformer. This is followed by a layer of insulation. The coil may be wound directly around the core, or it may be wound separately and inserted on the core. Various methods are used, but they are not described in the literature.

2. Input Materials - Raw materials for coil winding include conductors, conductor insulation, and layer and interlayer insulation. Wire is usually copper, nickel-clad or plated copper, silver-plated copper, anodized aluminum, or silver. Conductor insulation materials vary widely. It should be relatively thin to permit good coil space factors; have uniform high insulation strength along its length; be compatible with the impregnant; and permit winding by conventional methods with a reasonable amount of care.[8] Conductor insulations may be bakelite varnish, epoxy varnish, ceramic-coated Teflon, Teflon, silicone-treated glass fiber, Formex, Kel-F, polyurethanes, polyimides, nylon, polyvinyl chloride, polyester polyvinyl formyl, and oleoresing.[7,8] Insulation should be compatible with the winding and be capable of being impregnated, have sufficient mechanical strength to permit winding on a multiple winding machine, retain insulation resistance after creasing, be thin enough to permit a good working space factor, and have a nonslippery surface. Some materials used in this capacity include kraft paper, Mylar, Teflon, mica paper, split mica, fiberglass cloth, and glass paper.[8]

3. Operating Conditions - Coil and insulation winding is conducted at ambient temperature and atmospheric pressure.

4. Utilities - Electricity would be required for operation of winding machines.

5. Waste Streams - There are no air or water emissions associated with this process.

It is likely that scrap materials (e.g., insulation, metal from conductors) are generated during these operations.

6. Control Technology - Wire scrap is likely collected and sold for recycle. Insulator plastics could be recycled through the process or stored and landfilled.

Impregnation and Coating

1. Function - The impregnant or coating in coils serves to provide high electrical insulation between conductors; provide a mechanical bonding agent; assist in dissipating generated heat; and assist in environmental protection against dirt, moisture, oxygen, radiation, chemicals, etc. It should provide the necessary dielectric strength, be essentially void free, retain insulating properties and mechanical strength for the expected usage, impregnate thoroughly, and be compatible with other materials. A variety of materials and processes are used.[7,8] Three examples are cited below which illustrate these differences.

One typical cycle cited for a silicone rubber impregnant used in coils for operation in the 100° to 150°C range is as follows:[8]

- Air-dry coil at 135°C for minimum of 8 hours.
- Cool for 1 hour in a tank at pressure of 5 mm mercury.
- Cover the coil with impregnant and, after 5 minutes, break the vacuum and allow the coil to remain in solution for 5 to 10 minutes.
- Air-dry at room temperature for 1 to 2 hours.
- Prebake at 75°C for 8 to 10 hours.
- Cure for 3 to 4 hours at 200°C.

For high-temperature applications (over 150°C), degassed silicone resins are often used. This must be applied in an oxygen-free atmosphere. Impregnation is followed by a pre-bake at 180° to 200°C for about 2 hours, then vacuum degassing at temperatures ranging from 200° to 600°C.[7]

Another material used to form a rigid coil structure that can be employed at very high temperatures is aluminum phosphate ($AlPO_4$). In this impregnation cycle, all organic material is removed from the assembled core and coil by degassing under a vacuum in an oven linearly programmed to reach 500°C within a 2-hour period. A pressure vessel is then filled with the required amount of $AlPO_4$ solution, and the coil and core is immersed. A 50 μm vacuum is drawn, held for 15 minutes, and followed by a 2-minute 6.9×10^5 Pa (100 psig) pressure. There are four additional cycles. The assembly is then removed, air-dried at room temperature for 12 hours, and cured for 2 hours at 125°C, 2 hours at 150°C, and 15 minutes at 500°C.[8]

A third cycle described in the literature is for DC-997, a silicone varnish offered by Dow Corning. This procedure is as follows:[8]

- Prebake coils at 200°C for 4 hours.
- Cool coils to 65°C for approximately 1 hour.
- Evacuate the coils for 15 minutes at a pressure of no more than 20 mm of mercury.
- Soak coils in impregnant for 1 hour.
- Drain and dry coils for 30 minutes.
- Bake at 200°C for 2 hours.
- Cool to room temperature.
- Dip, drain, and air-dry for 30 minutes.
- Bake 6 hours at 200°C.

2. Input Materials - Various types of materials may be used for impregnants; these include silicone resins, silicone rubber, refractory ceramics, phenolic varnishes, epoxies, nylons, mineral waxes, polyesters, polyvinyl formyl, and polyvinyl butyral.[7,8]

3. Operating Conditions - This process can cover a wide range of operating temperatures and pressures. Specific examples are presented in the discussion of the process function.

4. Utilities - Electricity is required for vacuum pumps, fan and blower motors, and pumps for moving impregnant materials. Natural gas would be required to heat ovens.

5. Waste Streams - Organic solvents or various other organic constituents of the impregnant material could be volatilized during curing and baking operations.

There are no wastewater effluents or solid wastes associated with this process other than unused and contaminated impregnant materials.

6. Control Technology - The use of controls for this process is not discussed in the literature.

Encapsulation

1. Function - The encapsulant provides additional protection against moisture, dirt, and chemicals, as well as resistance to thermal cycling and added mechanical strength. It should have sufficient dielectric strength to withstand voltage stresses and exhibit good adherence to coil and metal parts.[7,8] Casting and dipping are the usual application methods.

2. Input Materials - The most often used encapsulant materials are mineral- (mica, silica) or fiberglass-filled silicone rubber, polyester resins, and epoxies. Epoxies are used for temperature applications up to 200°C, whereas silicone rubbers are used for temperature applications from 200° to 300°C. Curing agents for epoxies are usually amine-based or an acid catalyst.[7]

3. Operating Conditions - Silicone resins require baking at 400°C for one hour.[7] Conditions for epoxy and polyester resin applications are not cited in the literature. These probably vary according to type.

4. Utilities - Electricity is required for operation of conveyor motors for dipping, for process controls, for operating molding machinery, heaters, and drying. Natural gas may also be used to heat ovens.

5. Waste Streams - Curing of silicone resins may generate some organic fumes, especially if a solvent is used to formulate the material. Details are not available.

There are no known liquid or solid wastes other than unused or off-spec or contaminated resins.

6. Control Technology - The use of air pollution control technologies for this process is not described in the literature.

Epoxies, polyester resins, and silicones are thermosetting plastics which cannot be reused. One survey of electronic component manufacturing plants indicated that wasted plastics were stored and hauled to landfills for disposal.[9]

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SECTION 6

PRINTED CIRCUIT BOARDS

INDUSTRY DESCRIPTION

Printed circuit (PC) boards consist of nonconductive board material onto which a circuit pattern of conductive metal has been formed. The board provides a surface for the application of a conductive wiring path and supplies support and protection for electrical components to be connected by the board circuitry.[1]

Printed circuit boards can be classified into three basic types: single-sided, double-sided, and multilayer. The type of board used for specific applications depends on such factors as spatial and density demands and intricacy of the circuits.[1]

Single-sided boards are used for relatively simple applications, where circuit types and speeds do not place unusual demands on the electrical characteristics of the wiring. When density demands require more than one layer of wiring, circuits are printed on both sides of the board. The interconnection between the layers is accomplished through the board rather than around it, and what are termed plated-through holes have come to be the conventional way of making such a connection. The holes thus serve a dual purpose, providing an electrical connection from one side of the board to the other and accommodating a component lead. These are, of course, more difficult to make than the single-sided boards because of the extra steps involved (drilling and through-hole plating).[1]

The necessity for increased wiring density in many electronic packaging applications can be met by the use of more than two layers of wiring in the form of a multilayer printed board. A multilayer board is a series of individual circuit board layers bonded together by an epoxy glass material. It is a monolithic assembly in which the internal and external connections to each level of the circuitry are determined by the system wiring program.[1]

Three main printed circuit board production methods have evolved over the years: the additive, subtractive, and semiadditive techniques. The additive technique involves electroless plating on unclad board materials to produce printed circuits, and is used to produce 5 to 10 percent of the annual industry production total. The subtractive technique involves the removal of a large amount of metal from metal-foil-clad board material to form the desired circuit pattern, and is the major processing method used in the industry. The semi-additive technique is a combination of the additive and subtractive techniques. Production begins with unclad boards which are metallized with electroless copper. This is followed by image transfer, pattern electroplating, and etching to remove unwanted copper as in the subtractive process.[1,2]

Raw Materials

Printed circuit boards are constructed of materials such as glass, ceramics, and plastics. Copper is the primary metal used for conductive circuitry, with nickel, gold, and rhodium in some applications. Solder (tin-lead) and tin are used to protect copper or other metals during the etching process.[1,2]

Other major processing materials include cleaners, resists (etchant resistive materials), adhesion promoters, catalysts, and etch solutions. These cover a broad range of formulations (many proprietary) of abrasives, acids, alkalis, chelating agents, organic solvents, etc., as described in the detailed process descriptions.[1,2,3]

Products

The Bureau of the Census classifies printed circuit boards into SIC 3679052. Electronic assemblies using circuit boards were initially developed for the demanding quality control requirements of the aerospace and computer industries, primarily on the West Coast. Currently, printed circuit boards are used in a broad range of products including business machines, computers, communication equipment, and home entertainment equipment. The most typically produced boards are two-sided or multilayered with plated-through holes. They are fabricated from glass-epoxy, flame-retardant rigid laminates and designed to accept all types of electrical components.

Table 6-1 shows estimated sales from 1978 through 1983 for various categories of printed circuit boards. These estimates represent industrywide consumption of boards shipped by domestic and foreign manufacturers for the U.S. market. Total annual board production is estimated to be about 14 million m^2.[1]

Companies

There are 327 plants involved in the manufacture of printed circuit boards. Total employment of these plants is approximately 20,600, while total production employment is estimated to be 11,900.[4] The domestic industry consists of large facilities totally involved with printed board manufacture, both large and small captive facilities, small job shops doing contract work, and specialty shops which do low volume and high-volume precision work. A few major companies involved in printed circuit board manufacture include TRW Cinch Graphik, Texas Instruments, Motorola Semiconductor, Microtran, GTE Sylvania, Western Electric, Rockwell International, Synthane-Taylor, Cincinnati Millacron, and Chicago Etching.

Environmental Impacts

Air emissions from printed circuit board manufacturing include particulates, acid and alkali fumes, and chlorinated organic solvent vapors. Particulates are generally released during board preparation operations. Acid fumes originate from solutions used in most wet processes. Chlorinated organic solvent vapors are primarily the result of board surface cleaning and preparation processes. Control of air emissions involves collection of contaminated air streams using hoods above processing baths. Contaminant removal is based on segregation and treatment of similar air streams.[2]

Total process water flow from printed circuit board manufacturing discharged to POTW's on a national basis is estimated to be 23 million liters per day. An average plant process water flow is estimated to be 70,800 liters per day.[4] The principal constituents of the liquid waste streams from printed circuit board manufacturing are suspended solids, copper, lead, fluorides, phosphorus, tin, palladium, and chelating agents.[1] A range of constituent

TABLE 6-1. PRINTED CIRCUIT BOARD SALES, $ MILLION[5]

Product	Year				Annual growth, %
	1978	1979	1980	1983	
Printed circuits (total)	532.5	611.0	669.0	834.0	13.8
Rigid boards (total)	474.0	548.5	602.0	743.0	13.8
Single-sided	70.0	76.0	76.0	86.0	6.5
Double-sided	253.0	277.5	302.0	359.0	10.9
Multilayer	151.0	195.0	225.0	298.0	20.1
Flexible circuits	58.5	62.5	67.0	91.0	13.2

concentrations found in end-of-pipe raw liquid waste streams from printed circuit board manufacturing is shown in Table 6-2.[1]

Low pH values are characteristic of the wastes because of the acid cleaning and necessary surface pretreatment. The suspended solids are primarily metals from plating and etching operations and dirt that is removed during the cleaning processes prior to plating. The large amount of copper present in the waste stream comes from both electroless copper plating and copper electroplating and etching operations. Fluorides are primarily the result of cleaning and surface treatment processes utilizing hydrofluoric and fluoroboric acids. Phosphorus results from the large amount of cleaning that is performed on the boards. Tin is released during catalyst application and solder electroplating; palladium is also a waste constituent from catalyst application. The chelating agents present are primarily from the electroless plating operations, although others may have been added by cleaning, immersion plating, and gold plating.[1]

The liquid wastes from printed circuit board manufacture may be controlled using end-of-pipe treatment systems. Alternatively, some plants segregate wastes into separate streams and treat each individually. Also, there are many commonly used in-line technologies for reducing pollutant concentrations, for reducing wastewater quantities discharged, for reclaiming potential pollutants for reuse, and for reusing water itself.[1] Generally, in-line treatment and separate treatment of segregated waste streams provide the most effective treatment of printed circuit board manufacturing wastes.

Solid wastes produced during printed circuit board manufacturing include sludges generated during treatment of liquid process wastes and particulates removed from dust collectors. Collected particulates typically contain fine printed circuit board materials, copper, and small amounts of inorganic metals from wear of board machining equipment. Sludges contain primarily metal hydroxides and other precipitates of spent processing chemicals; they may be dewatered and disposed on-site or contract hauled off-site. Metals and other chemicals recovery from sludges may also be practiced on or off-site.

TABLE 6-2. CHARACTERISTICS OF RAW WASTE STREAMS FROM PRINTED CIRCUIT BOARD MANUFACTURING[1]

Constituent	Range, mg/liter
Total suspended solids	0.998 - 408.7
Cyanide, total	0.002 - 5.333
Cyanide, amenable to chlorination	0.005 - 4.645
Copper	1.582 - 535.7
Nickel	0.027 - 8.440
Lead	0.044 - 9.701
Chromium, hexavalent	0.004 - 3.543
Fluorides	0.648 - 680.0
Phosphorus	0.075 - 33.80
Silver	0.036 - 0.202
Palladium	0.008 - 0.097
Gold	0.007 - 0.190
EDTA	15.8 - 35.8
Citrate	0.9 - 1342
Tartrate	1.3 - 1108
NTA	47.6 - 810

INDUSTRY ANALYSIS

The following industry analysis considers each individual production operation (or series of closely related operations), called here a process, to examine in detail its purpose and actual or potentail effect on the environment. Each process is examined in the following aspects:

1. Function
2. Input materials
3. Operating conditions
4. Utilities
5. Waste streams
6. Control technology

There are three principal production methods for printed circuit boards: additive, subtractive, and semi-additive. These methods have many processes in common, and many combinations of processes are employed. The principal emphasis in the remainder of this section is on the subtractive processing sequence, which is the most commonly employed. Figures 6-1, 6-2, and 6-3 are flowsheets showing the processes used for each method, as well as their interrelationships and major waste streams.

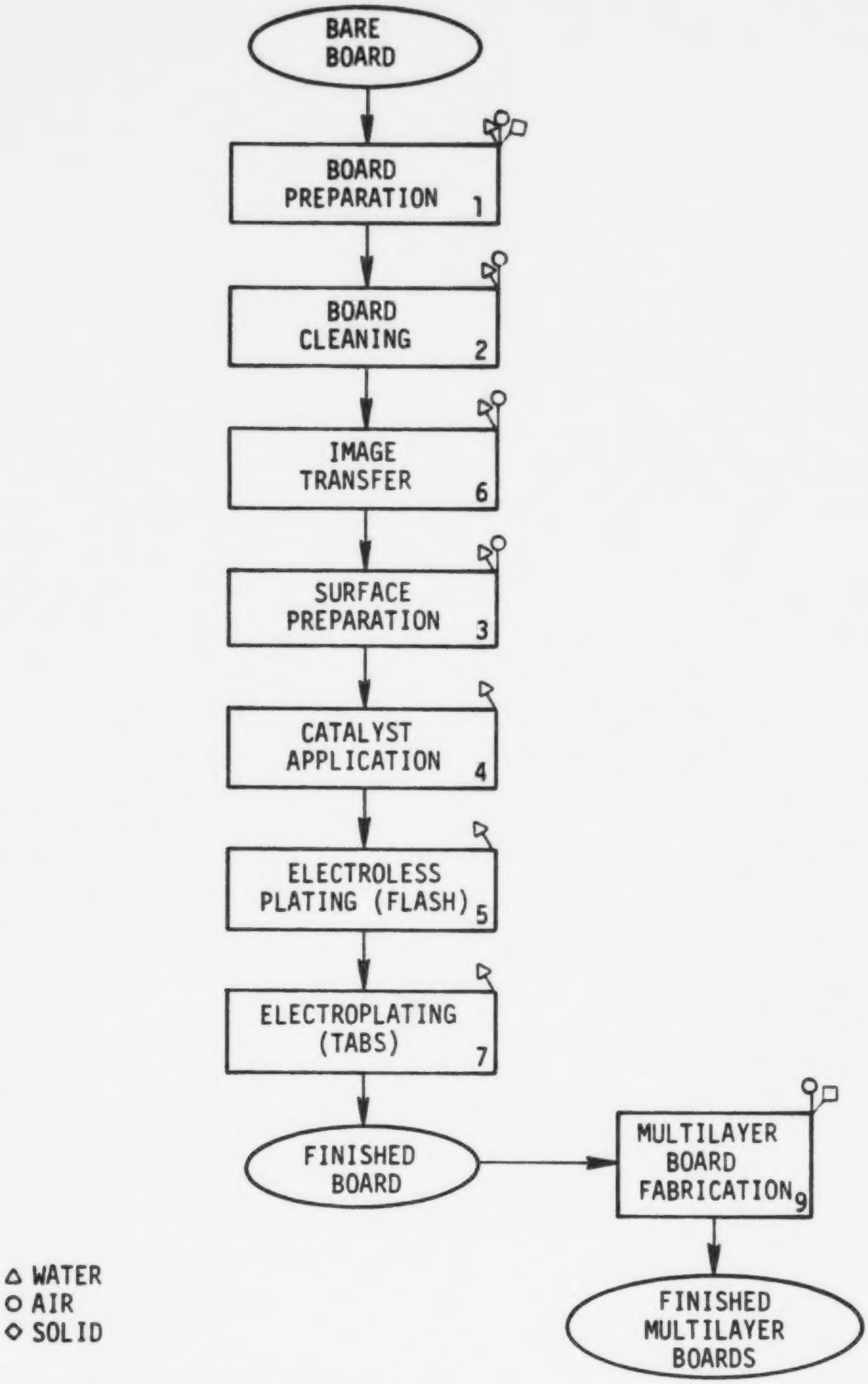

BARE BOARD
BOARD PREPARATION 1
BOARD CLEANING 2
IMAGE TRANSFER 6
SURFACE PREPARATION 3
CATALYST APPLICATION 4
ELECTROLESS PLATING (FLASH) 5
ELECTROPLATING (TABS) 7
FINISHED BOARD
MULTILAYER BOARD FABRICATION 9
FINISHED MULTILAYER BOARDS
△ WATER
○ AIR
◇ SOLID

Figure 6-1. Additive printed circuit board production flowsheet.

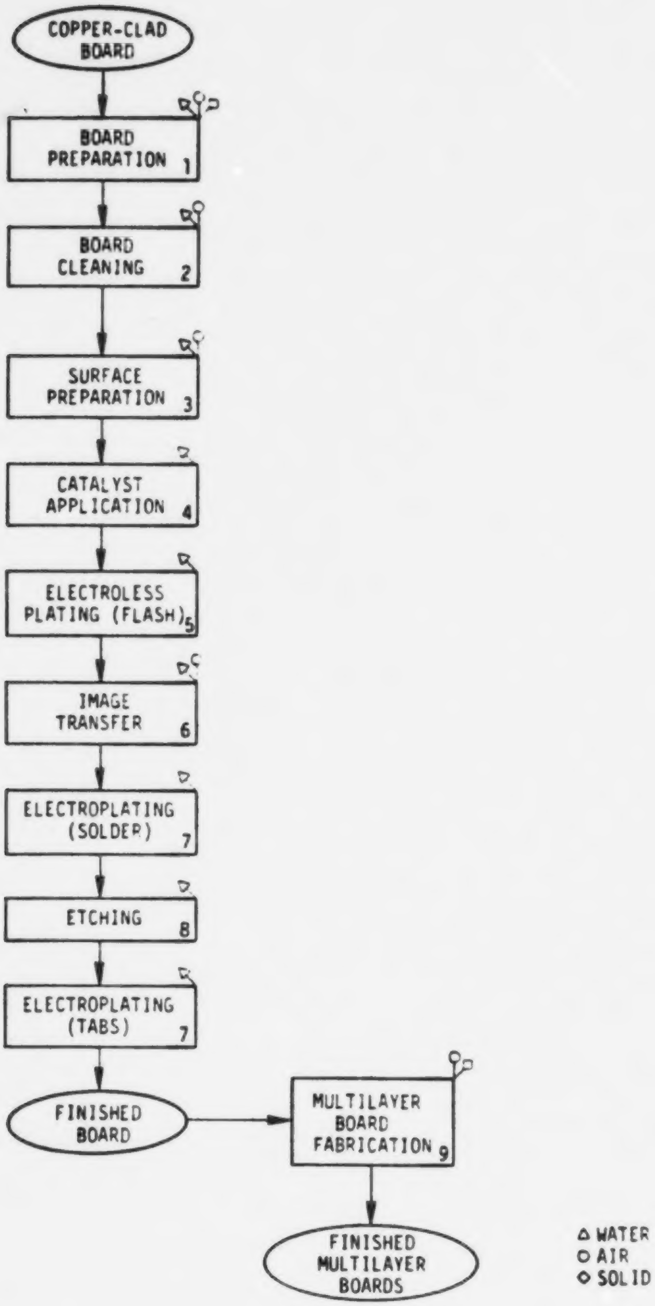
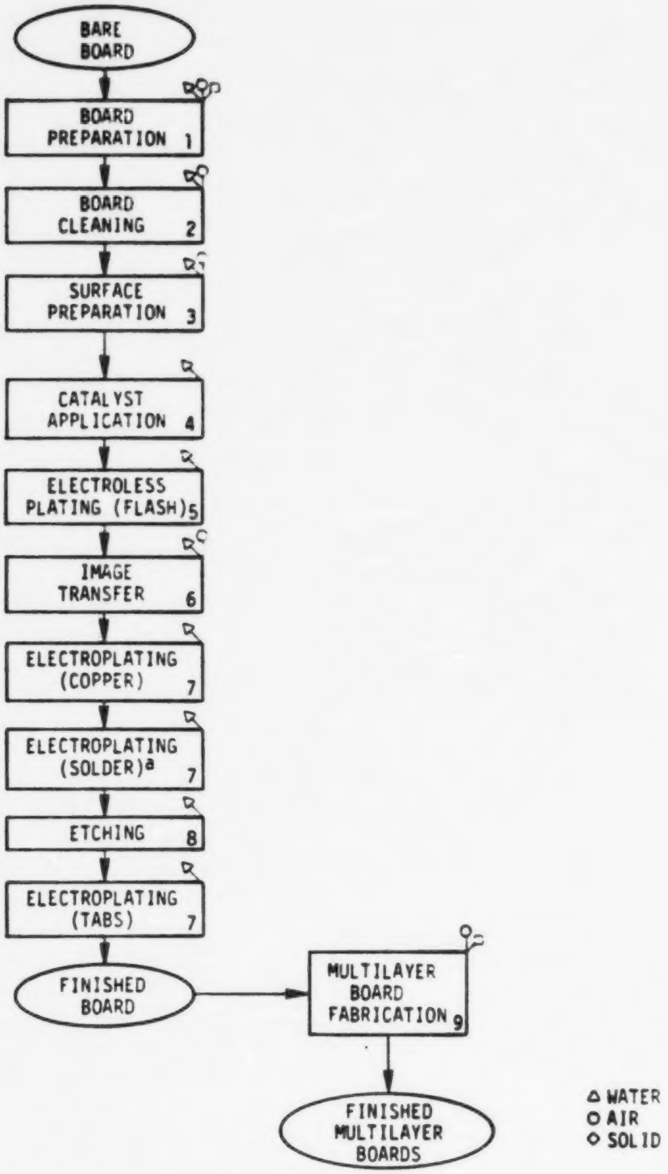

COPPER-CLAD BOARD
BOARD PREPARATION 1
BOARD CLEANING 2
SURFACE PREPARATION 3
CATALYST APPLICATION 4
ELECTROLESS PLATING (FLASH) 5
IMAGE TRANSFER 6
ELECTROPLATING (SOLDER) 7
ETCHING 8
ELECTROPLATING (TABS) 7
FINISHED BOARD
MULTILAYER BOARD FABRICATION 9
FINISHED MULTILAYER BOARDS
△ WATER
○ AIR
◇ SOLID

Figure 6-2. Subtractive printed circuit board production flowsheet.


BARE BOARD
BOARD PREPARATION 1
BOARD CLEANING 2
SURFACE PREPARATION 3
CATALYST APPLICATION 4
ELECTROLESS PLATING (FLASH) 5
IMAGE TRANSFER 6
ELECTROPLATING (COPPER) 7
ELECTROPLATING (SOLDER)a 7
ETCHING 8
ELECTROPLATING (TABS) 7
FINISHED BOARD
MULTILAYER BOARD FABRICATION 9
FINISHED MULTILAYER BOARDS
△ WATER
○ AIR
◇ SOLID

[a] Not required with negative image transfer method.

Figure 6-3. Semi-additive printed circuit board production flowsheet.

Board Preparation

1. Function - Individual or multilayer boards or laminates are sawed into blanks slightly larger than is desired for the finished product. Generally, a one-inch border is left on each edge to allow excess material for "tabs" and for board finishing.[1] Circular saws with carbide teeth are generally used for paper-base laminated boards. Diamond-steel-bonded saws are widely used for high volume glass-base laminates. Alternatively, entire boards or selected board areas may be die cut (blanked) or sheared to obtain the desired board size and shape.[2]

Board cutting is followed by hole drilling or punching in a predetermined pattern for mounting various electronic components.[1] At some plants, holes are drilled by computer controlled machines at rates of approximately 300 holes per minute, with hole location accuracies of ± 0.025 mm.[2] Next, the board is deburred on top and bottom surfaces by sanding and beveling, removing loose chips remaining from previous steps.[1] Hand sanders equipped with fine sandpaper or machines with composition abrasive brushes (operated either wet or dry) are used.[2] Other operations used to prepare boards for subsequent processes include routing and slotting. Board routing is performed to produce boards with superior edge finishes and closer tolerances than can be provided with shearing or sawing.[1,2]

2. Input Materials - Printed circuit boards are generally composed of nonconductive materials such as glass, ceramics, or plastics. The most common board materials are glass epoxy and phenolic paper. For the subtractive technique, raw printed circuit boards are copper-foil clad on one or both sides. Boards vary in thickness from 0.8 mm to 3.2 mm. Board sizes range from less than 1.3 cm square to 45 cm square. Typically, copper cladding is 305 g/m^2, with a range of 153 g/m^2 to 610 g/m^2.[1,2,3]

The National Electrical Manufacturers Association (NEMA) and the Federal government have standardized the characteristics of several commonly used copper-clad laminates:

NEMA Standard	Military Standard	Description
G-10	MIL-P-13949D, Type GE	General purpose glass fiber, epoxy laminate. Moisture resistant, excellent electrical and physical properties
G-11	MIL-P-13949D, Type GB	Similar to G-10 but better temperature stability
FR-4	MIL-P-13949D, Type GF	Similar to G-10 but flame-retardant
FR-5	MIL-P-13949D, Type GH	Similar to G-11 but flame-retardant

3. Operating Conditions - Generally, board preparation operations are performed at ambient temperatures. Operations on paper-base laminated boards are frequently performed at 32° to 38°C.[2]

4. Utilities - Machining requires electricity for operation of small equipment motors.

5. Waste Streams - Cutting, sanding, routing, drilling, beveling and slotting operations all generate airborne particulates. The particulates are composed of fine printed circuit board materials (i.e., paper, phenol, epoxy, polyester, and polyimide), copper, and small amounts of inorganic metals resulting from wear of saws, drills, and other equipment.

A liquid waste stream is generated when sanding operations are accompanied by a water flush. Varying amounts of printed circuit board and sanding materials are generally present in the flush water effluent.

The only solid wastes are scrap board materials from cutting, sanding, and machining operations.

6. Control Technology - Dust collection is required to protect employees and equipment from particulates. Cyclone separators and baghouses may be used to separate collected particulates from the exhaust air.[2]

Solid particles in the liquid waste stream are removed in solids traps or collected along with precipitates during subsequent treatment.

Board Cleaning

1. Function - As a result of such operations as board drilling and sanding during board preparation, there are numerous particulates, imperfections, and epoxy smears which must be removed to provide good plating adhesion. Printed circuit boards must therefore be cleaned to facilitate board plating without flaws. Improper board cleaning is probably the greatest source of problems in subsequent processes and is responsible for a wide variety of image and plating defects.[2]

Circuit boards are cleaned both mechanically and chemically. Mechanical cleaning consists of brushing holes, power rinsing, and air blasting. Power rinsing entails high-pressure jets of abrasive slurry oscillated across the board surface to remove particulates. This is followed by a water rinse and an air knife drying cycle.[6] The boards are then chemically cleaned to remove soil, fingerprints, smears, or other substances which cause plating flaws.[2] This includes an acid hole cleaning operation to remove particulates and any bonding epoxy which obstruct the holes.[1,6] Chemical cleaning may also include vapor degreasing, ultrasonic cleaning, and repeated dipping in chemical baths to obtain the desired results.[3]

2. Input Materials - Mechanical cleaning is generally accomplished with an abrasive slurry of water and pumice, followed by water rinses.[2,3] Various acid and alkaline compounds, as well as organic solvents, are used in chemical cleaning. Concentrated sulfuric acid (>90 percent), fluoroacetic acid, hydrofluoric acid, and other acids may be used to dissolve epoxy material. Organic solvents such as trichloroethylene, 1,1,1-trichloroethane, perchloroethylene, trichlorotrifluoroethane, and methylene chloride are widely used as surface degreasers. Alkaline cleaners contain sodium hydroxide and potassium hydroxide compounds.[1,2,3,6]

3. Operating Conditions - Organic solvents are used at temperatures ranging from 40° to 120°C. The two extremes are for special situations while the middle of the range is the most common. Available data indicate that acid solutions are used at ambient temperatures, while alkaline cleaning solutions are used at temperatures up to 65°C.[2,7]

4. Utilities - Electricity is required for direct immersion coil heating of baths, mechanical cleaning equipment motors, pumps, and blowers for bath agitation. Steam is required for vapor degreasing equipment and bath heating in large plants. Water is required for rinses.

5. Waste Streams - Air emissions consist of acid fumes and organic vapors from vapor degreasing. The fumes and vapors are usually not contaminated with other materials. Since different control technology is required, the two air emissions are kept separate.

Spent acid and alkaline solutions and rinses contain dissolved copper fluoride and/or resin. Spent organic degreasers and rinses contain organic contaminants (primarily from the solvents used).

There are no solid wastes from this process other than minor residues from mechanical cleaning.

6. Control Technology - Wet scrubbing is required to remove acid fumes from the air. The contaminated airstream is collected via chemical fume hoods and sent through ducts to a scrubber where it is contacted with either water or some other material which will absorb the fumes. The scrubbed air then passes on to the atmosphere and the absorbing solution is treated along with the other acidic waste streams. Chlorinated solvent fumes are collected via chemical fume hoods and then passed through a bed of activated carbon. The carbon bed is regenerated with steam to recover the solvent for reuse.[2]

Either batch or continuous treatment is used for pH control of acid and alkaline rinse waters and dumps of spent cleaning solutions. Alternatively, spent acid and alkaline baths are contract hauled for off-site disposal. pH adjustment of copper bearing rinse waters is frequently practiced to precipitate copper as an hydroxide. The precipitate is concentrated into a sludge and hauled away for disposal or recovery. Waste stream segregation and lime treatment are used to precipitate fluorides at pH 10 from cleaning bath rinse waters. Due to their high costs, recovery of spent chlorinated organic solvents from wastewater collection sumps is often economically attractive. Collected solvents separated by gravity are then recovered in-house or hauled away for reclaiming.

Surface Preparation

1. Function - In the additive and semi-additive production processes, unclad boards must undergo surface preparation to promote adhesion of a catalyst and electroless plating in subsequent process steps. To accomplish this, the boards are subjected to a mild chemical "etch" (not to be confused with Process No. 8) to make the surface of the boards microporous. This allows deep penetration of the catalyst and subsequent strong bonding of the electroless copper plate. It is followed by a water rinse. An acid dip follows to solubilize etched copper salts, then another water rinse, a final acid dip, and a final water rinse.[1,2,6]

Surface preparation for some unclad boards is initiated with the use of a "swell-and-etch" procedure. In this procedure, the top layer of board epoxy is swelled by use of a solvent system and then etched by a strong oxidizing medium. The same rinsing and acid dipping routine used with other boards is then followed. This procedure requires an extra thick epoxy surface; conventional unclad boards are unacceptable because etching would penetrate the fiberglass and degrade the board.[2]

There are also specially fabricated laminate boards that have preconditioned surfaces. The surfaces of these boards have, in essence, previously been micro-etched. As a result, the handling and disposal of solvents, strong oxidizers, and other special wastes are minimized.

Copper-clad boards used in the subtractive technique generally have an oxidation inhibitor on their surfaces. If the inhibitor is not completely removed, peeling will occur between the copper clad surface and the electroless deposit. To accomplish this, a light etch is usually given as a preventive measure.[2,3]

2. Input Materials - For the "swell-and-etch" procedure, strong organic solvents are used for swelling surfaces; these include trichloroethylene, 1,1,1-trichloroethane, and methylene chloride. Strong oxidizers are used as etchants for this procedure (mainly a mixture of sulfuric and chromic acids). For copper-clad boards, ammonium persulfate is the primary etchant used to remove the oxidation inhibitor. Hydrogen peroxide, sulfuric acid, and cupric chloride can also be used.[2,3]

3. Operating Conditions - No information was found regarding the temperature of solvent used in the "swell-and-etch" procedure. Strong oxidizers are used at 50°C, followed by rinse water at ambient conditions. Ammonium persulfate solutions are maintained at 20° to 45°C. Immersion times are approximately 2 minutes.

4. Utilities - Electricity is required for direct immersion coil heating of baths and blowers for bath agitation. Steam may be used for bath heating in large plants.

5. Waste Streams - Depending on the specific chemicals used in the process, air emissions will consist of acid fumes and organic solvent vapors. The fumes and vapors are usually not contaminated with other materials. Since different control technologies are required, the two air emissions are segregated.

Spent solvents, acid solutions, and rinsewater are generated during board preparation. The rinsewater will contain small amounts of solvents and acid. All liquid waste streams will also contain some dissolved board materials, including epoxy, phenolics, fiberglass, and dissolved copper from copper-clad boards.

There are no solid wastes reported from this process.

6. Control Technology - Wet scrubbing is used to remove acid fumes from the air. The contaminated airstream is collected via chemical fume hoods and sent through ducts to a scrubber where it is contacted with either water or some other material which will absorb the fumes. The scrubbed air then passes on to the atmosphere and the absorbing solution is treated along with the other acidic waste streams. Chlorinated solvent fumes are collected via chemical fume hoods and then passed through a bed of activated carbon. The carbon bed is regenerated with steam to allow solvent recovery.[2]

Either batch or continuous treatment is used for controlling pH from acid rinsewaters and dumps. Spent solvents and acids can be contract hauled to disposal sites, or sent to recycling plants for regeneration and recovery. Systems incorporating activated carbon adsorption are also available to recover solvents "in-house." The high cost of chlorinated solvents makes recovery an economically attractive alternative. Ammonium persulfate control is discussed in Process No. 8.

Catalyst Application

1. Function - Catalyst application is the deposition of a thin layer of palladium on board surfaces to be electroless plated. Catalyst deposition is necessary for electroless copper to plate onto the exposed plastic of a bare board in the next process for the additive and semiadditive techniques, and for through-hole plating in the subtractive technique.[1] Printed circuit boards are immersed in a solution of stannous chloride (30 g/liter) and hydrochloric acid (30 g/liter) followed by immersion in a solution of palladium chloride (0.25 g/liter) and hydrochloric acid (1.0 g/liter).[2] A reaction takes place with the adsorbed stannous chloride leaving a layer of palladium metal on the surface as the catalyst. Catalyst application is not necessary for copper-clad boards used in the subtractive process.

2. Input Materials - Stannous chloride, hydrochloric acid, and palladium chloride are required for this process. Water is used for rinses between immersion in the different solutions.[1,6]

3. Operating Conditions - Immersion time in the palladium chloride solution is usually 2 to 10 minutes. Stannous chloride solution immersion time is approximately 1 minute. Palladium chloride and stannous chloride baths are maintained at room temperature.

4. Utilities - Electricity is used to power miscellaneous pumps and motors and compressors or blowers that provide air to agitate baths.

5. Waste Streams - There are no air emissions reported from this process.

Spent stannous chloride baths and rinsewater will contain dilute hydrochloric acid generated as a by-product of adsorbing tin on the board surface. Stannic oxide is contained in spent palladium chloride baths and rinsewater as a result of the substitution reaction between tin and palladium.[1]

There are no solid wastes from this process.

6. Control Technology - pH adjustment and clarification are used to control tin and palladium discharges from catalyst application waste streams to less than 1.0 and 0.5 mg/liter, respectively.[4]

Electroless Plating (Flash)

1. Function - Electroless plating metallizes nonconductive surfaces without the use of the outside power source that is required for electroplating (electroless baths contain their own source of electrons for current flow). Catalyzed printed circuit boards are immersed in electroless copper solution for the additive and semi-additive techniques and for through-hole plating in the subtractive technique. Thicknesses of electroless copper deposits range from 0.25 μm to 2.5 μm. Deposition rates are commonly 0.03 to 0.04 μm/min, but recent formulations have been able to give 0.1 μm/min. The ideal deposit will be dense, fine-graded, and oxide free.[2,3] Following the electroless bath, the boards are spray or counterflow rinsed with water and acid rinsed to neutralize the residual alkaline film from the electroless bath. This is followed by another water rinse. Next, the boards are dried by air, heat, or chemical displacement of water. Mechanical scrubbing is also used to condition the surface of the plated metal for further processing.[1,6]

There are several optional steps which a printed circuit board may undergo as part of the electroless plating operation. After the above operations, the printed circuit board must be thoroughly dried to prevent the electroless deposit from oxidizing. An oxidized deposit results in voids or microfine pits in the electroless coating which have a detrimental effect on image transfer quality. Drying can be accomplished in hot air ovens, or by immersion in a water displacing liquid, followed by immersion in a vapor degreaser and evaportion of solvent.[2,3] The printed circuit board may also undergo mechanical scrubbing in order to precondition the surface of the board for image transfer and electroplating. The procedure is the same as mechanical scrubbing (Process No. 1) although not as aggressive. After scrubbing, the board must be rinsed and dried, as above.[6]

Immediately following the electroless copper plating operation, printed circuit board manufacturers commonly flash panel-plate boards before the final rinsing and drying. The flash is used to maintain the integrity of the electroless deposit from either oxidation or subsequent etching. This is accomplished by either panel or pattern electroplating solder over the electroless plate. Panel plating consists of copper plating the entire board area (including holes). In pattern plating, only holes and circuitry are copper plated. The flash applies a minimum of 0.025 mm of copper.[2]

2. Input Materials - Typically, electroless copper baths contain copper sulfate with a mixture of sodium carbonate or sodium gluconate, Rochelle salts, Versene-T, sodium hydroxide, and formaldehyde (37 percent), as described in Table 6-3.[7] Copper, formaldehyde, and sodium hydroxide are consumed in the electroless plating process and must be replenished periodically.[2] Other metals which can be electroless plated include gold, silver, lead, iron, cobalt, nickel, chromium, arsenic, antimony, and alloys of nickel with either tungsten, phosphorous, or boron.[3] Only a few of these are commonly used in printed circuit board manufacture. The acid rinse usually contains sulfuric acid (2 to 20 percent by volume), although other acids can be used. The panel-plate flash consists of a copper pyrophosphate plating solution.[2]

3. Operating Conditions - Most electroless baths operate in the range of 21° to 27°C. Too low a temperature can result in a bath that plates slowly or not at all. Too high a temperature can cause the chemicals to decompose or cause a runaway reaction.[3] Electroless baths commonly operate in the pH range of 11 to 12.[2] Rinses and baths are maintained at ambient temperatures.

4. Utilities - Electricity is required for direct immersion coil heating of baths, blowers or compressors for bath agitation, and miscellaneous pumps or motors.

5. Waste Streams - There are no air emissions reported for this process.

Liquid waste streams generated include spent electroless copper solutions, rinsewater contaminated by dragout, and spent acid rinsewater. These streams will contain acids and complexed copper.

There are no solid wastes reported for this process.

6. Control Technology - Complexed copper cannot be removed by pH elevation and precipitation. Heating or the addition of a catalyst is required to initiate copper precipitation and collection as a sludge. An alternative removal method is to add acid to the electroless copper solution to lower the pH to 5 to 8, causing the copper to precipitate. Yet another method involves heating and lowering the pH, followed by addition of caustic and sodium hydrosulfite to form a copper oxide precipitate. It is estimated that effluent

TABLE 6-3. TYPICAL ELECTROLESS COPPER PLATING BATHS[7]

	Bath 1	Bath 2
Copper sulfate	29 g/liter	25 g/liter
Sodium gluconate		60 g/liter
Sodium carbonate	25 g/liter	
Rochelle salts	140 g/liter	
Versene-T	17 g/liter	
Sodium hydroxide	40 g/liter	20 g/liter
Formaldehyde (37 percent)	150 g/liter	25 g/liter
pH	11.5	11.5
Temperature	21°C	24°C

copper concentrations can be reduced to 1.4 mg/liter copper or less, with typical removals of approximately 88 percent.[2]

Distillation may also be used to recover electroless copper for reuse, while the extracted water can be used as rinse make-up water. Using this process, recovered copper concentrations of 21,800 mg/liter have been reported for a wastestream initially containing 416 mg/liter. Extracted make-up water copper concentration was approximately 3 mg/liter.

Image Transfer

1. Function - Image transfer is a series of steps designed to produce a circuit pattern on a printed circuit board. Specific methods used to create and transfer the circuit pattern image vary depending on circuit density, product volume to be produced, and manufacturing techniques.[1] In the simplest method (subtractive), a copper-clad board is coated with the exact circuit pattern using a protective resist material to create a positive image on the board. In a subsequent step (Process No. 8), the unprotected copper areas (not covered by the protective resist) are chemically etched away to remove unwanted copper from the board. A second method (additive) involves creating the reverse or negative pattern on a board by using a resist that leaves the desired circuit pattern uncovered. The uncovered areas are later cleaned and plated.

There are three principal methods in which the image or circuit pattern is actually transferred to the board: screening, photosensitive resist methods, and offset printing. There are two principal types of resist: those which are cured by exposure to ultraviolet light (photo-sensitive resist) and those which are cured by drying (thermal resist). Screening consists of selectively applying resist material through the open areas of a stencil or screen. The screen is stretched tightly over a metal frame, which is then placed over the board. Ink or resist material is then squeezed through the screen to produce either a positive or negative pattern. Another type of resist that is screened onto the board, which is applied "dry," is a thermoplastic material made fluid by passing through an electrically heated screen. The resist then solidifies on contact with the board into a nearly dry print. The screening method is useful for simple low density circuits because its comparatively low cost allows for high volume production.[1]

Photosensitive resist (photoresist) is applied by dipping or rolling a pattern onto the board. The photosensitive resist is a light sensitive polymer which, after curing, has a significant chemical resistance. Copper-clad boards usually go through a prebake cycle before exposure. The resist is then exposed to ultraviolet light through the pattern. The light sensitive material hardens and the unexposed resist material is removed. This is followed by baking or curing the resist to allow it to withstand plating solutions. This type of masking has made possible the production of high density and intricate circuits because of the precision obtainable.[1]

Offset printing, similar to a printing press, is applicable to high volume production. An etched plate (the printing plate) serves as the master pattern. After the plate is inked, the ink image is deposited on the copper-clad board. By making several passes, enough ink can be built up on the board to form a plating or etching resist. The same types of resists mentioned earlier can be used for offset printing.[1]

For all image transfer methods, excess or unexposed resist is washed away with solvent, rinsed, and allowed to dry. The boards are then soaked in an alkaline cleaner to remove any lingering resist and rinsed again. Copper-clad boards, as a final step, are immersed in a tank of copper adhesion promoter, rinsed, immersed in an acid solution, and rinsed one last time before being electroplated.[6]

2. Input Materials - For the screening image transfer method, screens are either silk, polyester, or stainless steel. Screening inks are composed of oil, cellulose, asphalt, vinyl, or other resins.[1]

Photosensitive resists are light-sensitive solids, available as either liquids or dry solids. They can be divided into two broad categories, positive and negative, with the latter used most often in circuit boards because of their high chemical resistance, good image reproduction qualities, and low cost. The basic components of resists are resins, sensitizers, additives, and solvents. Although they do not necessarily have to be photosensitive, resins must be capable of being rendered insoluble upon reaction with the sensitizer. The major resins used for negative photoresists include polyvinyl cinnamate, allyl ester resins, and isoprenoid resins. Sensitizers are added to provide or increase photosensitivity. Commonly used sensitizers include thiazoline compounds, azido compounds, nitro compounds, nitroaniline derivatives, anthrones, quinones, diphenyls, azides, xanthone, and benzil. Additives may be added to photoresists, especially those which are polyvinyl cinnamate-based, for a number of reasons: to increase adhesion; to reduce swelling during development; to prevent formation of a scum layer; and to prevent darkening.

Table 6-4 lists some additives used in production of photoresists.[8] Solvents are added to resist formulas for dissolution purposes during storage and application. Common resist solvents include orthoxylene, metaxylene, paraxylene, toluene, benzene, chlorobenzene, cellosolve and cellosolve acetate, normal butyl acetate, 1,1,1-trichloroethane, acetone, methyl ethyl ketone, and methyl isobutyl ketone.

Offset printing resists include many of those used in screening or photosensitive application. Solutions to remove excess resist are generally trichloroethylene, stabilized chlorinated hydrocarbons, mixtures of alcohol and Stoddard solvent, xylene, commercial developing solutions, acetone, ketones, esters, and alkali-based solutions.

3. Operating Conditions - Conditions vary with the particular resist that is applied. Precuring temperatures vary from 45° to 120°C. Precuring requires approximately 15 minutes. Developing temperatures range from ambient to 90°C, while developing times range from 30 seconds to 4 minutes or longer if thick resist coats are used. To complete the curing, some resists require baking at 120°C for 15 minutes.[2]

4. Utilities - Electricity is required to provide heat for oven precuring, developing, and curing.

5. Waste Streams - Depending on the processing method and the specific chemicals used, air emissions will consist of various organic compounds.

Liquid waste streams are made up of water rinses containing chlorinated hydrocarbon and batch dumps of spent chlorinated solvents. No other information on copper or resist streams is available in the literature.

There are no solid wastes reported for this process.

6. Control Technology - Organic compounds fumes are collected and passed through activated carbon beds.[2]

The organic solvents and resists are immiscible with and heavier than water. By routing all organic contaminated streams to one sump, the solvent can be separated by gravity and collected for recovery or disposal.[2] In some instances solvent recovery using distillation may be feasible.

TABLE 6-4. ADDITIVES USED IN PHOTOSENSITIVE RESISTS

1. To prevent scumming
    - A. Stabilizers
        - Phenol
        - Hydroquinone
        - Catechol
        - Resorcinol
        - o-tert-Butyl-p-methoxy phenol
        - Phenyl-β-naphthylamine
        - p-Hydroxyphenylmorpholine
        - p-Phenylenediamine
    - B. Acids
        - Cinnamic acid
        - Benzoic acid
        - Phenylacetic acid
        - Hydrocinnamic acid
        - Chloroacetic acid
        - Salicylic acid
        - Crotonic acid
2. To prevent darkening
    - A. Citric acid
    - B. Tartaric acid
    - C. Oxalic acid
3. To prevent polymerization
    - A. Hydroquinone
    - B. Pyridine
    - C. Copper resinate
    - D. Cuprous chloride
    - E. Nitrobenzene
    - F. β-napthol

Electroplating

1. Function - Electroplating is the process of depositing a metallic coating on a board by immersing it in a conductive bath that utilizes an external electrical power source to provide the driving force. The conductive bath is usually water containing metal ions in solution. Printed circuit boards may be electroplated with several different metals, one upon the other. Between each electro-coat, the boards are rinsed, and after the last coat, thoroughly rinsed and dried.[2,3,6] Electroplating is performed at several junctures in the production of printed boards. It is employed in the actual build-up of the circuit (in the additive and semi-additive processes); it applies the anti-corrosive layer to the circuit; and it is used to cover the tabs of all boards.[1]

To build up the circuit in the additive and semi-additive processes, copper electroplating is used, followed by either solder or tin electroplating.[1] The solder plate or tin plate acts as a mask during the etching process which follows electroplating, and secondly, protects the copper circuit from corrosion. Printed circuit boards frequently receive an immersion tin coating, which is applied over both copper and solder plating. The coating is temporary over copper plate, as it will oxidize. Over solder plate, the coating prevents oxidation of lead in the solder during processing with strong etchants.[2]

For the additive and semi-additive processes, the tabs go through a solder strip operation before tab plating to promote adhesion. This step is not required in the additive process. Those tabs that require nickel or gold plating, or both, are processed after the board is etched (Process No. 8). The tab electroplating process is the same as described above.

2. Input Materials - Table 6-5 presents the plating bath constituents that are used for plating specific metals.[2,3,7]

3. Operating Conditions - Table 6-6 presents common operating conditions for the plating baths mentioned above.[2,3,7] Many other plating baths are used but not described in the literature. These include hexavalent chromium-based solutions.

TABLE 6-5. PLATING BATH CONSTITUENTS[2,3,7]

Metal

A. Copper

1. Specifications for a Copper Pyrophosphate Bath

Component	Concentration, g/liter
Copper metal, Cu^{+2}	22-38
Pyrophosphate, $P_2O_7^{-4}$	150-250
Oxalate	15-30
Nitrate, NO_3	5-10
Ammonia, NH_3	1.5-3
Orthophosphate, HPO_4^{-2}	No more than 1.3 to 1.7

2. Specifications for Acid-Copper Sulfate Baths

Component	Standard concentration, g/liter	High throwing power concentration, g/liter
Copper sulfate, $CuSO_4 \cdot 5H_2O$	160-300	60-90
Copper, Cu^{+2}	40-75	15-22.5
Sulfuric acid, H_2SO_4	52.5-135	187.5-225
Addition agents	As required	
Chloride ion	20-80 ppm	

3. Specifications for a Acid-Copper Fluoroborate Bath

Component	Concentration, g/liter
Copper fluoroborate, $Cu(BF_3)_2$	224-448
Copper metal, Cu^{+2}	60-120
Fluoroboric acid, HBF_4 (free)	10.5-30
Boric acid, H_3BO_3	15-30
Addition agents	As required

B. Solder (tin-lead)

1. Specification of Standard Solder (60 percent tin, 40 percent lead) plating bath

Component	Concentration, g/liter
Stannous tin	56.2
Lead	26.2
Free fluoroboric acid	100.0
Free boric acid	26.2
Peptone	5.2

(continued)

TABLE 6-5 (continued)

2. Specification of High-Throwing-Power Solder (60 percent tin, 40 percent lead) Plating Bath

Component	Concentration, g/liter
Stannous tin	15.0
Lead	10.0
Free fluoroboric acid	400.0
Free boric acid	21.6
Peptone	5.2

C. Nickel

1. Typical Nickel Sulfamate Plating Bath

Component	Concentration, g/liter
Nickel sulfamate, $Ni(SO_3NH_2)_2$[a]	300-525
Nickel metal, Ni	60-120
Boric acid, H_3BO_3	30-45
Nickel bromide, $NiBr_2$[a]	11-19

2. Modified Watts Nickel Plating Bath

Component	Concentration, g/liter
Nickel sulfate, $NiSO_46H_2O$	225-375
Nickel metal, Ni	50-84
Boric acid, H_3BO_3	30-45
Nickel bromide, $NiBr_2$[a]	11-19
Stress reducer	As needed

D. Tin-Nickel

1. Specifications for a Tin-Nickel Plating Bath

Component	Concentration, g/liter
Stannous chloride, $SnCl_2$	48.8
Tin (stannous tin), Sn	26-38
Nickel chloride, $NiCl_2$	300
Nickel, Ni	68-83
Ammonium bifluoride, NH_4HF_2	41.0
Total fluorine[a]	34-45

(continued)

TABLE 6-5 (continued)

E.	Tin	1.	Specifications for a Bright Acid Tin Plating Bath	
			Component	Concentration, g/liter
			Stannous sulfate, $SnSO_4$	30
			Tin metal, Sn	13.5-15.6
			C.P. sulfuric acid, H_2SO_4	184
			Brighteners	Per vendor instructions
F.	Gold	1.	Specifications for a Typical Acid Gold Bath	
			Component	Concentration, g/liter
			Gold metal as potassium gold cyanide	4-16
			Conductivity salts	As necessary
			pH-adjusting salts	As necessary
		2.	Specifications for a Typical Alkaline Noncyanide Gold	
			Component	g/liter
			Metallic gold content	6-16
			Conductivity salts	As necessary
			Reagent grade sodium hydroxide	To raise pH
			Reagent grade sulfuric acid	To lower pH
G.	Rhodium	1.	Specifications of a Rhodium Sulfate Bath	
			Component	Concentration
			Rhodium sulfate	1.3-2.1 g/liter
			Sulfuric acid	25-35 ml/liter
		2.	Specifications of a Rhodium Phosphate Bath	
			Component	Concentration
			Rhodium phosphate	2.1 g/liter
			Phosphoric acid	40-80 ml/liter

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[a] U.S. Patent 3,554,878.

TABLE 6-6. COMMON OPERATING CONDITIONS FOR PLATING BATHS[2,3,7]

Bath type	pH	Temperature, °C
Copper pyrophosphate	8.1-8.8	43-60
Acid-copper sulfate	strongly acid	18-50
Acid-copper fluoroborate	0.2-1.7	18-50
Standard solder	≤ 0.5	18-38
High-throwing-power solder	≤ 0.5	18-38
Nickel sulfamate	2.5-4.2	24-60
Modified watts nickel	2.5-4.2	24-60
Tin-nickel	1.5-2.5	38-70
Bright acid tin	proprietary	13-24
Acid gold	12	24-38
Alkaline noncyanide gold	3.5-4.5	20-50
Rhodium sulfate	proprietary	40-54
Rhodium phosphate	proprietary	40-54

4. Utilities - Electricity is required for direct immersion coil heating of baths, blowers or compressors for bath agitation, direct current for plating, and miscellaneous pumps and motors. Steam may be used for bath heating at large plants.

5. Waste Streams - There are no air emissions reported for this process. Waste streams consist mainly of rinses and contaminated or spent dumps of plating solutions. These streams will contain copper, nickel, lead, fluoride, and possibly other metals, as well as inorganic chemicals found in plating solutions (e.g., cyanides for processes using gold or copper cyanide plating solutions).

There are no solid wastes reported for this process.

6. Control Technology - Rinse waters containing heavy metals such as copper, nickel, and lead (if not complexed) can be precipitated as hydroxides by proper pH adjustment and settling. Chromium wastes must first be reduced from the hexavalent to the trivalent state. Cyanide-containing wastes must first be oxidized using chlorine or other strong oxidants. Fluorides can be partially removed by treating with lime to precipitate calcium fluoride at pH 10. Since calcium fluoride is somewhat soluble, it is generally advantageous to segregate fluoride wastes in a separate solids removal system.[2] It is estimated that effluent copper concentrations can be reduced to 0.2 mg/liter or less. Nickel and chromium removals of approximately 85 percent or greater have been regularly reported, with final chromium concentrations of 0.05 mg/liter or less. Cyanide destructions using chlorine oxidation of greater than 99.5 percent with remaining cyanide concentrations of less than 0.1 mg/liter are also reported. Typical concentrations following sedimentation for copper, chromium (trivalent) and nickel are 0.49, 0.54 and 1.10 mg/liter, respectively.[1]

Removal data shown in Table 6-7 have been developed with pH adjustment and precipitation, followed by diatomaceous earth filtration.[1] The resulting sludges are typically contract hauled for metals recovery or disposal.

Additional metals recovery techniques include reverse osmosis, ion exchange distillation, and electrolytic methods. Reverse osmosis may be used for treatment and/or recovery of nickel or copper from acid plating solutions. Ion exchange may be used for nickel or gold recovery or for rinsewater treatment (as shown in Table 6-8).[1] Distillation technology has been used to

TABLE 6-7. DIATOMACEOUS EARTH FILTRATION PERFORMANCE DATA[1]

Parameter	Removal, %	Raw wastestream, mg/liter	Effluent wastestream, mg/liter
TSS	98	524	10
Cr(+3)	95	12.2	0.611
Fe	96	5.81	0.248
Cu	94	7.53	0.444
Ni	95	2.57	0.044

TABLE 6-8. ION EXCHANGE PERFORMANCE DATA[1]

Parameter	Raw rinsewater, mg/liter	Treated effluent, mg/liter
Cr	7.60	0.06
Cu	4.45	0.09
Fe	3.70	0.10
Ni	6.20	0.00
Ag	1.50	0.00
Sn	0.50	0.00
CN	0.80	0.20
SO_4	21.0	2.0
PO_4	3.75	0.80

recover copper at 21,800 mg/liter and chromium at 27,500 mg/liter from feeds initially containing 416 and 5060 mg/liter, respectively. Process condensates generally contained less than 3 mg/liter of the metal being removed.[1]

The fate of other inorganic chemicals in the plating solutions was not found in the literature. Generally, spent electroplating baths, if they cannot be regenerated, are contract hauled for disposal or incineration.

Etching

1. Function - Etching is the process by which all unwanted copper (that other than in the circuit) is removed from the board. Most manufacturers employ mechanical etchers which spray etch solutions, solder brighteners or activators, and rinsewaters onto horizontally traveling boards. Etching is always used in the subtractive technique, while an abbreviated etch is employed in the semi-additive technique.[1]

An etch solution is then sprayed onto the boards; this is followed by a rinse, mechanical scrub, another rinse, and thorough drying.[6] Selection of etchants and resist strippers is based on board design, cost, pollution problems, and type of resist.

2. Input Materials - Resist stripping solutions which oxidize and decompose resist consist of sulfuric-dichromate, ammoniacal hydrogen perioxide, metachloroperbenzoic acid, and others. Resist removal is also accomplished by the use of commercial strippers which swell the resist, making it soft enough to be scrubbed or washed off. Commercial strippers are composed of methylene chloride, methyl alcohol (10 percent by volume), furfural, and phenol (1 percent by volume). Other strippers use various ketones, chlorinated hydrocarbons, non-chlorinated organic solvents, and 2 to 10 percent sodium hydroxide. Resists may also be removed by high-temperature firing or boiling in sulfuric or benzene sulfonic acids, but neither of these procedures is practical for conventional boards.[2,3]

Commonly used etchants are ferric chloride, ammonium persulfate, chromic acid, cupric chloride, and alkaline etches.[1] Tables 6-9 to 6-13 show the compositions and variations of these etch solutions.[2]

3. Operating Conditions - Etching solutions are maintained between 35° and 55°C depending on the particular etchant, and pH varies between 7.8 to 9.2. Temperatures used for resist stripping range from ambient to 60°C. High-temperature firing to remove resist is carried out at 400° to 500°C.[2,3]

TABLE 6-9. CHARACTERISTICS OF $FeCl_3$ SOLUTIONS[a][2]

	Low strength	Optimum	High strength
Percent by weight	28	34-38	42
Specific gravity	1.275	1.353-1.402	1.450
Baume	31.5	38-42	45
g/liter	365	452-530	608
Molarity	2.25	2.79-3.27	3.75

[a] Data taken at 20° to 25°C. Photoengraving $FeCl_3$ 42° Baume has 0.2 to 0.4 percent free HCl; proprietary etchants contain up to 5 percent HCl.

TABLE 6-10. COMPOSITION OF TYPICAL PERSULFATE ETCH SOLUTIONS[2]

	Solution		
Component	1	2	3
$(NH_4)_2S_2O_8$	240 g/liter	240 g/liter	
$Na_2S_2O_8$			360 g/liter
$HgCl_2$	5 ppm	5 ppm	5 ppm
X-134[a] (optional)	120 g/liter	120 g/liter	120 g/liter
H_3PO_4		15 ml/liter	15 ml/liter

[a] FMC Chemical Corp.

TABLE 6-11. COMPOSITION OF TYPICAL CHROMIC-SULFURIC ACID ETCH SOLUTIONS[a][2]

Component	Solution	
	1	2
CrO_3	240 g/liter	480 g/liter
Na_2SO_4	40.5 g/liter	
H_2SO_4 (96 percent)	180 g/liter	31 ml/liter
Copper		4.9 g/liter

[a] Proprietary agents contain wetting, antiforming, and chelating agents, and catalysts.

TABLE 6-12. COMPOSITION OF TYPICAL CUPRIC CHLORIDE ETCH SOLUTIONS[2]

Component	Solution		
	1	2	3
$CuCl_2 \cdot 2H_2O$	2.2 M	2.2 M	0.5-2.5 M
HCl (20° Baume)	8 ml/liter	0.5 N	0.2-0.6 M
NH_4Cl			2.4-0.5 M

TABLE 6-13. COMPOSITION OF TYPICAL ALKALINE ETCH SOLUTIONS, mol/liter[2]

Component	Solution		
	1	2	3
NH_4OH	3.0	6.0	2-6
NH_4Cl	0-1.5	5.0	1.0-4.0
Cu (as metal)		2.0	0.1-6.0
$NaClO_2$	10.375		
NH_4HCO_3	0-1.5		
$(NH_4)_2HPO_4$		0.01	0.05-0.5
NH_4NO_3	0-1.5		

4. Utilities - Electricity is required for direct immersion coil heating of baths, blowers or compressors for bath agitation, high-temperature firing ovens, and miscellaneous pumps and motors. Steam may be used for bath heating in large plants.

5. Waste Streams - There are no air emissions reported for this process. Spent etchant and rinsewaters contain copper with either ammonia, chromium, or iron also present. Rinsewaters from resist removal will contain chlorinated hydrocarbons. The fate of the other resist stripping solutions and etchants is not described in the literature.

There are no solid wastes reported for this process.

6. Control Technology - Heavy metals such as copper, chromium, and iron (if not complexed) can be precipitated as hydroxides by adjusting the pH with caustic or lime addition. Chromium treatment is accomplished in two steps. First, hexavalent chromium is reduced to trivalent chromium using sulfur dioxide, sodium bisulfite, or hydrazine at pH 3 or less. Following this step, trivalent chromium can be precipitated as a metal hydroxide as described above. Several copper removal and recovery techniques and effluent levels achievable are described in Process No.'s 5 and 7.

Several methods are available for treating ammonium persulfate and copper: removal by copper electrodeposition, precipitation of copper by reaction with scrap aluminum and sodium chloride, and precipitation of copper hydroxide after removal of ammonia with alkali and heat. Other ammonia removal methods include phosphoric acid addition followed by lime addition to precipitate heavy metal ammonium-phosphates, hydroxides, and other insoluble compounds.

The strippers and resists are heavier than and immiscible in water.[2] These materials can be collected in a sump for recovery and disposal.[2] Etchants may be recovered using distillation, reverse osmosis, ion exchange, or electrolytic methods.

Multilayer Board Lamination

1. Function - Multilayer boards consist of individual printed circuit boards that have been bonded together and interconnected. Individual boards that are to be laminated together have circuits imprinted in the same manner as single- and double-sided boards.

The first step in the lamination process is the baking of laminates to remove water, solvents, and chemicals used in earlier cleaning steps. This assures that delamination will not occur. Next, semicured sheets of glass-epoxy (called B-stage) are sheared and punched to match the size and shape of the circuit panels being laminated. The sheets of B-stage are used as the adhesive to bond circuit layers together. The circuit boards are stacked together, with sheets of B-stage laid in between the boards in a press containing registration pins to maintain circuit panel alignment. Application of heat and pressure to the laminate press follows; this converts the semicured B-stage material between circuits to fully cured C-stage epoxy. During the process, the B-stage resin becomes a liquid adhesive which fills all circuit pattern voids and bonds the layers together. Registration pins are then pushed out and the top press plate is removed. Excess epoxy is removed from the perimeter of the lamination and plugged racking holes are drilled out. The laminate is then baked to assure final cure for the laminate bond resin.[2]

2. Input Materials - Sheets of B-stage are available in standard G-10 and FR-4 material (described in Process No. 1). These sheets are semicured glass-cloth-reinforced epoxy resin. The epoxy resin, however, has not fully polymerized. Multilayer boards are fabricated almost exclusively from G-10 and FR-4 glass-filled epoxy boards. Other boards contain resins of polyimide, polyphenylene oxide (PPO) and glass-base Teflon.[2,3]

3. Operating Conditions - Lamination heating rate and final temperature are specified by the B-stage supplier. Temperatures vary from 150° to 230°C, and molding pressure averages 35 kg/cm^2. Molding times are approximately one hour. The board must be allowed to cool, under pressure, to at least 50°C before it can be removed from the press.[2,3] The operating conditions of the final curing oven are not described in the literature.

4. Utilities - Lamination presses are either electrically or steam heated.

5. Waste Streams - Resin volatiles are evolved during oven during and laminate pressing from final curing of B-stage resin.

There are no liquid waste streams from this process.

Glass-epoxy solid matter is produced when trimming excess epoxy from the boards.

6. Control Technology - Resin volatiles are handled the same as other organic vapors. They are collected by hoods and passed through activated carbon beds to adsorb the organic contaminants.[2]

Control techniques for solid glass-epoxy matter were not found in the literature.

REFERENCES FOR SECTION 6

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SECTION 7

ELECTRON TUBES

INDUSTRY DESCRIPTION

Electron tubes are devices in which electrons or ions are conducted between electrodes through a vacuum or ionized gas within a gas-tight envelope. The envelope may be made of glass, quartz, ceramic, or metal. This category includes receiving-type tubes for radio and television use, and transmitting, industrial, and other special-purpose tubes.

Electron tubes depend upon two basic phenomena for their operation: emission of electrons by certain elements and compounds when the energy of the surface atoms (or gaseous atoms in the case of gas discharge tubes) is raised by the addition of heat, light photons, kinetic energy of bombarding particles, or potential energy; the control of the movement of these electrons or ions in gas discharge tubes by the force exerted upon them by electric and magnetic fields. The use of electron tubes is based upon the controlled flow of electrons they produce. Receiving-type electron tubes are used primarily for low-voltage and low-power applications. These include radio and television receivers and electronic control and measuring equipment. Transmitting and special-purpose tubes include a variety of devices:

- High-vacuum tubes - diodes, triodes, multi-grid anodes.
- Gas and vapor tubes - e.g., thyratrons (used for "triggering" a current).
- Klystrons (ultrahigh-frequency current).
- Magnetrons (microwave frequencies).
- Traveling wave tubes.
- Light sensing tubes - camera tubes, image intensifiers and converters, photomultipliers.
- Light emitting devices - storage tubes, special display devices.

Electrodes are usually made of nickel mounted on a base glass or metal envelope. The tube is evacuated to 10^{-3} mm of mercury and the electrodes and/or the envelope are heated to remove unwanted gases. The passage between the tube and pumping system is sealed off and a getter material (usually magnesium, calcium, sodium, or phosphorus) previously introduced into the evacuated envelope is flashed by applying an electric current to the electrodes for several seconds. The getter material condenses on the inside surface and adsorbs any gas molecules. The vacuum within the tube increases progressively until an equilibrium value of 10^{-6} mm is reached.[1]

Due to the increasing use of semiconductors for applications that were previously filled by electron tubes, the manufacture of some types of tubes has dropped off sharply in recent years. Total shipments for receiving tubes have decreased from 162.2 million units in 1972 to 60.9 million units in 1977, and the total value of shipments over that same period has fallen from $182 million to $104.6 million.[2]

Raw Materials

Raw materials required for electron tube manufacture include glass envelopes, Kovar and other specialty metals, tungsten wire, and copper wire. They can be classified into five major categories:[1,3]

- Conductors - Copper and steel base materials with various plated surfaces such as copper, nickel, gold, aluminum, silver, and chromium are used extensively. These materials are good conductors and/or supporting mediums, are easily shaped and formed, and are cost-effective.

- Leads - Copper and nickel are the most common material for electron tube leads. Often the leads are a simple extension of one of the conducting electrodes.

- Encapsulating materials - Glass, ceramics, and various metals such as steel are used for electron tube encapsulating materials. They provide overall structural strength and assure integrity of the applied vacuum or gas filling.

- Inert gases - Electron tubes may either be filled with special inert gases such as neon, argon, and krypton, or they may be completely evacuated. Either method provides a dielectric medium of a predetermined resistance to the flow of electrons.

- Getters - Metals or mixtures of metals used in bulk getters include thorium, titanium, cesium, zirconium, magnesium, calcium, sodium, phosphorous, uranium, tantalum, hafnium, niobium, lanthanum, and other rare earth elements. These metals, which are deposited by evaporation on the walls of the glass or metal, adsorb gas molecules that come in contact and thus maintain a high vacuum throughout the life of the device.

Products

The analysis in this section includes the manufacture of receiving-type electron tubes for radio, television, and other electronic applications (SIC 36711), and transmitting and special-purpose tubes (SIC 36713). It excludes cathode ray picture tubes (SIC 36712) and cathode-ray tubes for industrial and military use (SIC 3671385), which are covered in Section 3.

Applications for receiving-type electron tubes are rapidly being replaced by solid state semiconductor devices. This is evidenced by the 57 percent decrease in shipments of receiving tubes over the period from 1972 to 1977.[2] Table 7-1 presents Census Bureau data which shows the decline in this industry.[2] An industry source reported total value of shipments by domestic and foreign manufacturers for the U.S. market at $111.6 million in 1978.[4] Estimates of the value of consumption of receiving-type electron tubes for 1979, 1980, and 1983 were reported to be $104, $96, and $34 million, respectively.[4] The annual decline from 1979 through 1983 is estimated to be 24.4 percent.[5]

Table 7-2 presents information on sales of transmitting and special-purpose electron tubes for 1972 and 1977.[2] Although incomplete, these data indicate that many of these devices also face declining or at best relatively stable markets.

Companies

The 1977 Census of Manufactures reports that 11 companies were involved in the manufacture of receiving-type electron tubes and 43 in the manufacture of transmitting and special-purpose tubes.[2] Because all types of electron tubes were categorized together, it is not possible to obtain information on the size of the establishments by total employment from Census Bureau data. Major manufacturers include General Electric, Westinghouse, GTE Sylvania, RCA, Amperex, and International Components Corporation.[6,7]

TABLE 7-1. RECEIVING-TYPE ELECTRON TUBE MANUFACTURERS AND PRODUCT SHIPMENTS[2]

Product	Number of companies	1972		1977	
		Product shipments		Product shipments	
		Quantity, million	Value, $ million	Quantity, million	Value, $ million
Receiving tubes, except cathode ray:					
As reported in the Census of Manufactures	11	a	189.6	a	104.0
As reported in Current Industrial Reports MA-36N, selected electronic and associated products, including telephone and telegraph apparatus	6	162.2	182.0	60.9	104.6

[a] Not applicable.

TABLE 7-2. TRANSMITTING AND SPECIAL-PURPOSE ELECTRON TUBE PRODUCT SHIPMENTS[2]

Product	1972		1977	
	Product shipments		Product shipments	
	Quantity, thousands	Value, $ million	Quantity, thousands	Value, $ million
Power and special tubes:				
High-vacuum tubes	4855.0	75.5	2112.3	73.7
Gas and vapor tubes	3973.2	32.3	8471.0	33.7
Klystrons	122.3	44.3	a	48.1
Magnetrons	168.3	35.5	192.3	52.9
Traveling-wave tubes	22.9	68.6	22.8	90.3
Light-sensing tubes:				
Camera tubes	a	a	a	36.0
Image intensifiers and converters	a	a	49.8	30.0
Photomultipliers and others	a	a	310.7	21.2
Light-emitting devices:[b]				
Storage tubes	a	a	16.0	19.0
Special display tubes	a	a	a	74.5
Miscellaneous other	a	11.0		

[a] Not available.

[b] Does not include CRT's for industrial and military purposes.

Environmental Impacts

There are few details in the literature concerning emissions from the manufacture of electron tubes. No significant air or solid waste streams are identified. The majority of water usage is for electroplating and part cleaning. Water effluents may therefore contain suspended solids, metals, and acids. These wastes may be adequately controlled using end-of-pipe treatment systems; there are many technologies that would be applicable. Recovery of metals or other chemicals from wastewater treatment sludges could be practiced on- or off-site.

INDUSTRY ANALYSIS

The following industry analysis considers each individual production operation (or series of closely related operations), called here a process, to examine in detail its purpose and actual or potential effect on the environment. Each process is examined in the following aspects:

1. Function
2. Input materials
3. Operating conditions
4. Utilities
5. Waste streams
6. Control technology

Only limited data are available in the literature on electron tube manufacture. This industry analysis covers two segments, receiving-tube and transmitting tubes. Figures 7-1 and 7-2 are flowsheets showing the processes used for manufacture of these devices, as well as their interrelationships and waste streams.

Insufficient data were found in the literature to allow preparation of individual process descriptions for the transmitting tube segment. The metal components destined to be used in construction of the tube are first cleaned in an unspecified solution and then electroplated with various metals (e.g., copper, gold, silver). Some of the finished metal components may be brazed to glass components to form a metal-glass envelope. The envelope is washed in an alkali or alcohol bath before proceeding to the tube assembly process, where additional finished metal parts and the tube envelope are assembled into the

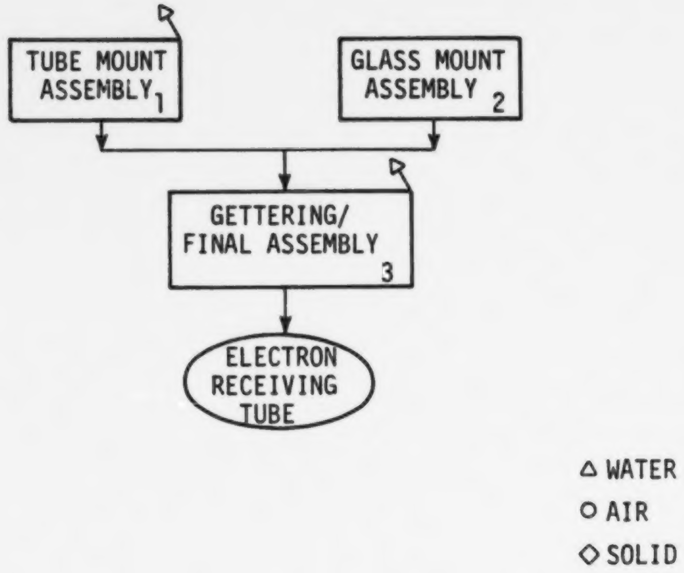
TUBE MOUNT ASSEMBLY 1
GLASS MOUNT ASSEMBLY 2
GETTERING/ FINAL ASSEMBLY 3
ELECTRON RECEIVING TUBE
△ WATER
○ AIR
◇ SOLID

Figure 7-1. Receiving-type electron tube production flowsheet.

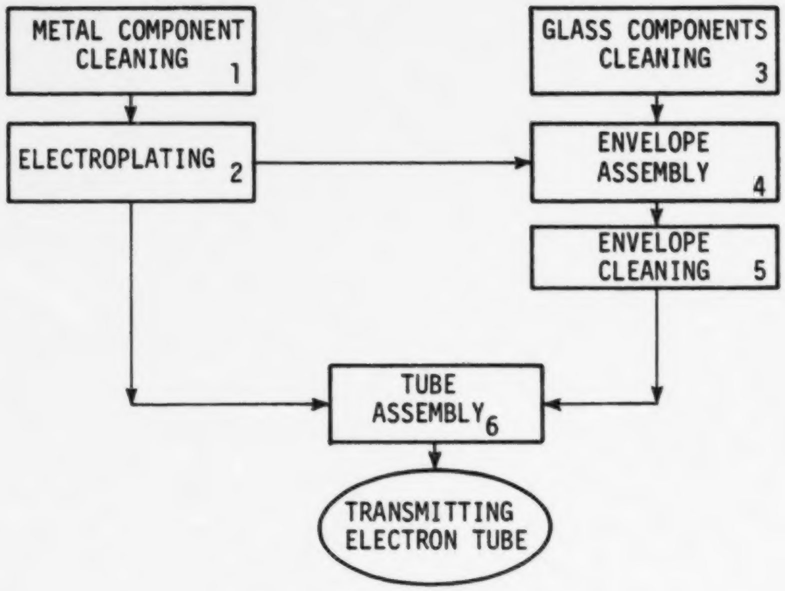
METAL COMPONENT CLEANING 1
ELECTROPLATING 2
GLASS COMPONENTS CLEANING 3
ENVELOPE ASSEMBLY 4
ENVELOPE CLEANING 5
TUBE ASSEMBLY 6
TRANSMITTING ELECTRON TUBE

Figure 7-2. Transmitting electron tube production flowsheet.

finished product. The final assembly stage may include various combinations of welding, soldering, annealing, and curing operations. The finished tube is then tested and packaged for shipment. Depending upon the exact type of tube being produced, the production sequence may or may not include the envelope assembly and cleaning steps (Process No.'s 4 and 5 on Figure 7-2).

Tube Mount Assembly

1. Function - Metal components used in the construction of tube grids and anodes are cut and machined to specified dimensions. The cutting process is most commonly performed using electron beam techniques. The machining involves physical (abrasive), chemical (electrolytic deplating), or electron beam evaporation methods. The metal parts are first cleaned in solvents, hot alkaline, or acid baths depending upon the type of metal being cleaned and the contaminant being removed. Next, the clean metal parts are "fired" in hydrogen or in vacuum bell jars to reduce further oxidation. The finished metal parts are then assembled into what is described as the tube mount assembly.[1]

2. Input Materials - The major inputs to the tube mount assembly consist of specialty metals electroplated with copper, nickel, chromium, gold, or silver. Dielectric material (mica) is used for spacers and to insulate the tube components. Additional materials used during the plating and cleaning operations include acids such as hydrofluoric, hydrochloric, sulfuric, and nitric; electroplating solutions containing conductive metals like gold, silver, copper, nickel, and chromium; and organic solvents such as methylene chloride and trichloroethylene.

3. Operating Conditions - The exact temperatures and pressures developed during the various operations of the tube mount assembly process are not reported. A majority of the operations are probably performed under ambient conditions, with the known exceptions being the metal cleaning and hydrogen "firing" steps.

4. Utilities - The cutting, machining, and assembling steps of this process require various forms of utility service, but the exact types and quantities are unknown.

5. Waste Streams - The extent of air emissions, if any, are not reported in the literature.

The majority of the water used in this process is for electroplating and cleaning of tube parts. The composition of waterborne waste streams is unknown.

The only solid wastes from this process would be minor amounts of scrap materials from cutting and machining operations.

6. Control Technology - The type of controls used in this process are not documented in the literature.

Glass Mount Assembly

1. Function - To form a glass mount assembly, the cathode, grid, anode, and cathode lead wires are sealed in an annealed glass base. The sealing operation is performed by a "glass mounting" machine. The entire component is then heat treated by baking in an oven.[1]

2. Input Materials - The cathode element of a receiving tube can be constructed from various thermionic materials including tungsten or tungsten alloys, and platinum with metal oxide coatings of barium, nickel, or iron. The encapsulation materials are most commonly glass, but can also consist of ceramic or metal, depending upon the structural strength required and the vacuum to be maintained.

3. Operating Conditions - The exact temperatures and pressures developed during the operations of the glass mount assembly process are unknown. A majority of the operations are probably performed under ambient pressures.

4. Utilities - The metal to glass sealing operation and the glass tube heat treatment require utility service, but the exact type and quantity are unknown.

5. Waste Streams - There are no documented air, water, or solid waste streams generated during this process.

6. Control Technology - The controls used in this process are unknown.

Gettering/Final Assembly

1. Function - Gettering describes the process by which the non-reactive nature of electron tube gases is maintained. Gettering is a process by which chemically active metals are evaporated on the surface of the vacuum tube enclosure, the grid work, the anode, or the cathode.

The finished electron tube is physically evacuated before the interior of the tube is coated with getter. Following the gettering operation, the final tube assembly is completed by addition of the tube base. The reactive getter metals added during the assembly preserve the non-reactive integrity of the tube vacuum or inert atmospere by removing oxygen or oxidizing species from the tube interior. Upon completion of the electron tube, the glass exterior is rinsed and the finished tube is aged, tested, and packaged.[1]

2. Input Materials - Barium is the most common metal used in gettering. Calcium, strontium, magnesium, aluminum, thorium, titanium, cesium, zirconium, and various other metals are also used. Glass, ceramics, and metals are used for tube encapsulating materials.

3. Operating Conditions - The exact temperatures and pressures developed during the sealing and evacuation procedures are unknown. The rinsing operation is probably conducted under ambient conditions.

4. Utilities - The rinshing operations will require some level of water service. This and the remaining operations will also require some additional quantity of electrical service.

5. Waste Streams - There are no known air emissions associated with this process.

The glass tube and bulb rinsing do not require a chemical cleaning process and as a result will produce an effluent discharge with little if any chemical pollutants.

There are no solid wastes from this process.

6. Control Technology - The controls used in this process, if any, are not reported in the literature.

REFERENCES FOR SECTION 7

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4. Components: Unaggressive Growth in Store. Electronics. January 3, 1980.

5. Predicasts Forecasts - 1980. Annual Cumulative Edition Issue No. 80. 4th Quarter. July 24, 1980. Predicasts, Inc.

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SECTION 8

CATHODE RAY TUBES

INDUSTRY DESCRIPTION

Cathode ray tubes (CRT's) are special purpose vacuum tubes in which a stream of electrons is focused onto a small area of a fluorescent screen, producing a luminous spot. The focused beam of high-velocity electrons can be deflected to allow any area of the screen to be scanned. The number of electrons in the stream at any instant of time is varied by electrical impulses corresponding to the transmitted signal. Most CRT's manufactured are used in televisions.

CRT's consist of four major components: glass envelope, glass face panel, steel aperture mask, and electron gun assembly.[1] The face panel is made of a special composition of glass which minimizes optical defects and provides electrical insulation for high voltages. The glass bulb is designed to withstand 3 to 6 times the force of atmospheric pressure. The glass face panel is a phosphorus-coated light-emitting screen at the front of the tube. The phosphor coating is applied to form small elemental areas, and in color picture tubes each is capable of emitting light in one of the three primary colors (red, green, blue), based upon the phosphor applied to that area. The image is viewed through this panel. An electron gun produces a stream of high velocity eletrons which is aimed and focused on the panel by static and dynamic convergence mechanisms and an electro-magnetic deflection yoke. An aperture mask behind the face of the screen blocks portions of the beam, allowing the unblocked portions to be focused on the panel. This allows phosphor excitation in specific areas of the panel. Some color picture tubes use three electron guns, one for each primary color. Commercially available aperture mask tubes are manufactured in a number of sizes.

Raw Materials

The raw materials for CRT production include conductors, leads, encapsulating materials, masks, phosphors, protective coating materials, graphite coatings, and solders:[1,2,3]

- Conductors - Copper and steel are the major base conductive materials used in CRT's.
- Leads - Copper and nickel are most often used. The leads are often simply extensions of the conducting electrodes.
- Encapsulating materials - Glass, ceramics, and various metals such as steel are used as encapsulating materials. They provide overall structural strength and assure integrity of the applied vacuum. Special glass is used for television picture tubes to enhance optical and electrical characteristics.
- Mask - The aperture mask which allows electron beams to strike the phosphor selectively in a color television picture tube is almost always made from steel.
- Photosensitive materials - A photosensitive solution is used to prepare the glass surface for phosphor application. It commonly contains dichromate, alcohol, and other proprietary substances. Developer solutions often are composed of hydrogen peroxide and/or deionized water.
- Phosphors - Common phosphor materials used in color picture tubes include cadmium sulfide, zinc sulfide, yttrium oxide, and europium oxide. The red phosphor is a rare earth phosphor in which yttrium oxide is activated with europium ($1/2O_3$: Eu(111)). The blue phosphor compounds are zinc and sulfide phosphors activated with silver (ZnS:Ag). The green phosphors are composed of zinc-cadmium sulfide activated with copper (Zn,(Cd)S:Cu). Many proprietary processes are used in applying these materials as red, green, and blue phosphors to the glass panel.
- Protective coatings - Toluene-based lacquer and silicate coatings are commonly applied to seal the phosphor coatings in place and protect them from damage.
- Graphite coatings - Slurries of carbon and a suitable binder are applied to the surfaces of the panel and envelope to prevent reflection and secondary emission of electrons, and to provide a conductive coating on the vacuum side of the glass envelope.
- Solders - The four basic parts of a CRT are held together with various solders; lead solders are the most commonly used.

Products

The Bureau of the Census classifies CRT's into two SIC codes: 36712 - color and black-and-white television picture tubes; and 3671385 - CRT's produced for military and industrial applications. The 1977 Census of Manufactures reports that 7.7 million new CRT's for color televisions and 733,000 CRT's for industrial and military applications were shipped in 1977.[4] No figures were given for new black-and-white television tubes.

Companies

There are 23 companies which manufacture CRT's for television and 13 involved in producing CRT's for military and industrial applications. A breakdown of the manufacturers of television tubes is presented in Table 8-1.[4] Major producers include RCA, GTE Sylvania, General Electric, Motorola, Westinghouse, Amperex, Clinton, Raytheon, and ITT.[5,6]

Environmental Impacts

As is the case with electron tubes, there are few data available in the literature concerning emissions during the manufacture of cathode ray tubes. There are no air emissions reported other than possible release of vapors from solvent degreasing tanks. Many steps in the manufacturing sequence do generate wastewater, however. These operations include degreasing and a variety of chemical cleaning, rinsing, and washing steps. The major wastewater pollutants can include metals, toxic organics, cyanide, oils and grease, phenols, fluorides, acids, and various proprietary photoresists and other solutions. These streams may be pH adjusted with lime, settled, and discharged to the environment or to municipal systems for futher treatment. Photoresist and developer solutions require special treatment to reduce their chromium content; this may be achieved by reduction from the hexavalent to trivalent state with sulfuric acid and sodium bisulfate, followed by further treatment with sodium carbonate, calcium chloride, and sodium bisulfate. Waste streams from phosphor application processes may be treated in separate settling and filtration systems prior to discharge.

TABLE 8-1. COMPANIES PRODUCING CRT'S FOR TELEVISIONS[4]

Product	No. of companies
New black and white TV's	2
Rebuilt black and white TV's	18
New color TV's:	
17 inch and under	4
18 and 19 inch	5
20 inch and over	5
Rebuilt color	25

The only sources of solid waste from cathode ray tube manufacture are scrap materials from various operations, including picture tube reclaim, and wastewater treatment sludges. Recovery of metals and other chemicals from the sludge can be practiced on- or off-site.

INDUSTRY ANALYSIS

The following industry analysis considers each individual production operation (or series of closely related operations), called here a process, to examine in detail its purpose and actual or potential effect on the environment. Each process is examined in the following aspects:

1. Function
2. Input materials
3. Operating conditions
4. Utilities
5. Waste streams
6. Control technology

The manufacture of cathode ray tubes is illustrated in this section by a discussion of color television picture tubes. Figure 8-1 is a flowsheet of these processes, as well as their interrelationships and waste streams.

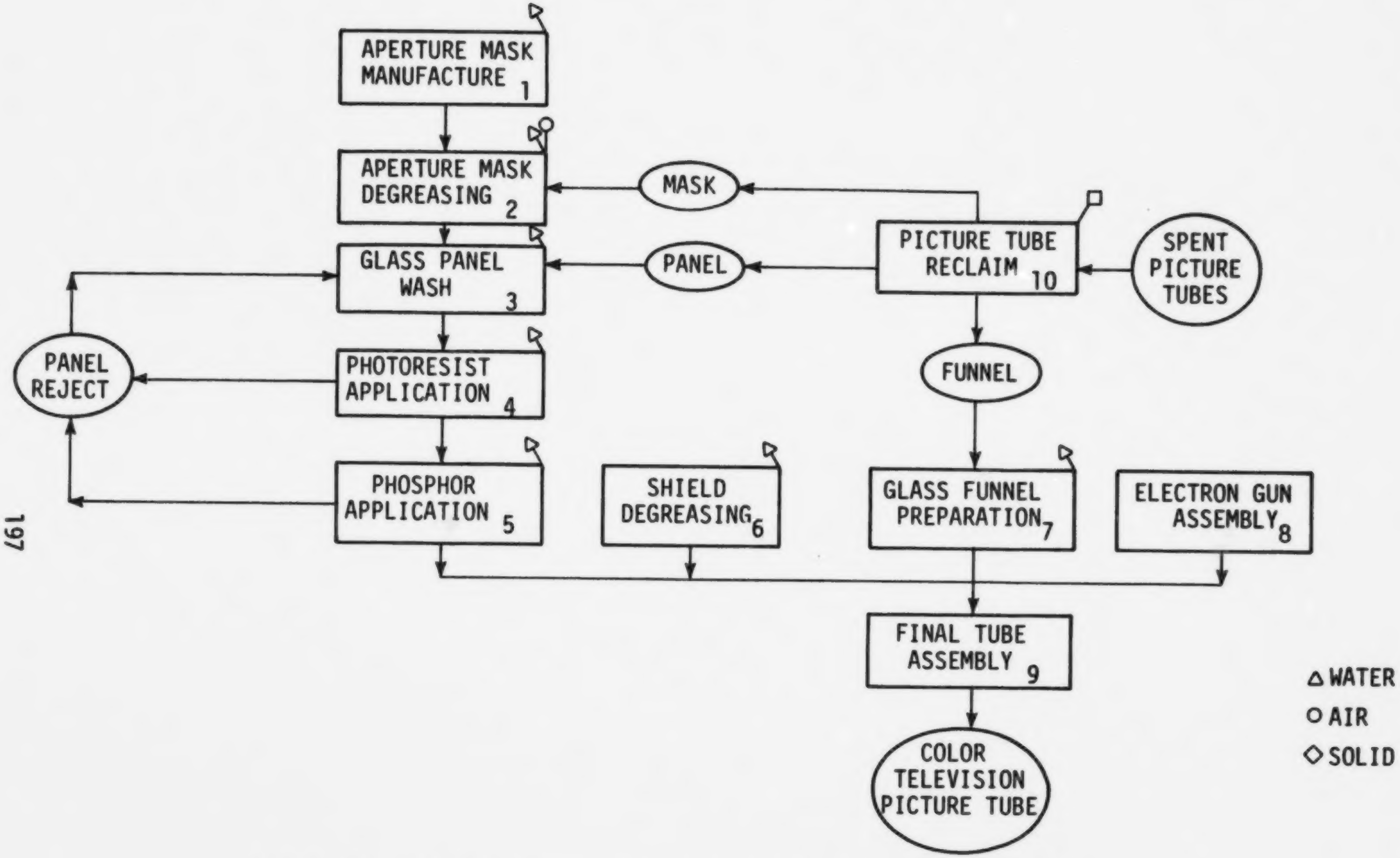
APERTURE MASK MANUFACTURE 1
APERTURE MASK DEGREASING 2
GLASS PANEL WASH 3
PHOTORESIST APPLICATION 4
PHOSPHOR APPLICATION 5
SHIELD DEGREASING 6
GLASS FUNNEL PREPARATION 7
ELECTRON GUN ASSEMBLY 8
FINAL TUBE ASSEMBLY 9
PICTURE TUBE RECLAIM 10
SPENT PICTURE TUBES
MASK
PANEL
FUNNEL
PANEL REJECT
COLOR TELEVISION PICTURE TUBE
△ WATER
○ AIR
◇ SOLID

Figure 8-1. Color television picture tube production flowsheet.

Aperture Mask Manufacturing

1. Function - Aperture masks used in conjunction with glass panels to produce the visual image are manufactured by fabricating the metal form, chemical cleaning, coating with a photosensitive material, etching, and rinsing. The holes produced in the aperture mask are the result of this etching, which is generally performed with ferric chloride. Aperture masks are generally manufactured at facilities separate from those involved in the actual construction of the CRT's.

2. Input Materials - The major structural material used for the manufacturing of aperture masks is steel. Additional substances involved in this process are chromium, zinc, ferric chloride, and proprietary photochemicals.

3. Operating Conditions - The exact temperatures and pressures encountered during the manufacturing of the steel aperture mask have not been documented.

4. Utilities - The type and quantity of utility service required for this process is unknown. Electricity is required to operate various machinery.

5. Waste Streams - There are no air emissions reported to be associated with this process.

The major waterborne pollutants include iron, chromium, zinc, ferric chloride, and particulate in the form of total suspended solids. In addition to these major pollutants, trace amounts of toxic contaminants have been identified in raw waste from an aperture mask manufacturing process. A summary of these substances is presented in Table 8-2.[1]

There are no solid wastes reported other than metal scrap.

6. Control Technology - The etching wastewater used during aperture mask manufacturing is pH adjusted with lime before being sent to a settling pond. The runoff from the settling pond is discharged directly into the environment.

TABLE 8-2. SUMMARY OF RAW WASTE DATA FROM AN APERTURE MASK MANUFACTURING OPERATION[1]

Substance	Concentration, mg/liter[a]
Toxic organics	
Methylene chloride	0.060
Toxic metals	
Cadmium	0.0002
Chromium	3.480
Copper	0.570
Lead	0.009
Zinc	0.193
Other pollutants	
Cyanide	2.1
Oil and grease	8.4
Total organic carbon	4.0
Biochemical oxygen demand (BOD)	18
Total suspended solids	52

Note: Data taken from a single operation.

[a] Single stream sample value.

Aperture Mask Degreasing

1. Function - Steel aperture masks are formed to the required size, solvent degreased, and oxidized.

2. Input Materials - Various industrial solvents are used to clean and degrease the steel apertures. Common solvents employed are methylene chloride, trichloroethylene, methanol, isopropanol, acetone, and polyvinyl alcohol.

3. Operating Conditions - The exact temperatures and pressures encountered during the aperture mask degreasing process have not been documented. It is assumed that this work is performed under ambient conditions.

4. Utilities - The types and quantities of utility service required for this operation are not reported.

5. Waste Streams - Degreasing operations may result in release of solvent vapors to the atmosphere.

Wastewater is produced during the operation of solvent recovery systems associated with the degreasing operation. A characterization of wastewater from two television picture tube manufacturing plants is summarized in Table 8-3.[1] Wastewaters are not segregated, so these pollutants could be introduced at any of several processes.

The generation of solid wastes during these operations is not reported.

6. Control Technology - Emissions from degreasing tanks can be reduced by increasing freeboard in the degreaser tank and using refrigerated chillers to create a cold air blanket above the solvent. Emissions can be controlled by the use of chillers or condensers and carbon adsorption.[7]

Wastewaters from the aperture mask degreasing are pH adjusted and settled. The literature describes a system in which this stream flows through three settling tanks prior to final discharge. All treated process wastewater, untreated process wastewater, and non-contact cooling water flow together to the municipal treatment system.[1]

TABLE 8-3. SUMMARY OF RAW WASTE FOR TELEVISION PICTURE TUBE MANUFACTURE[1]

	Plant A[a]				Plant B[b]
	Minimum concentration, mg/liter	Maximum concentration, mg/liter	Mean concentration, mg/liter	Flow-weighted mean concentration, mg/liter	Developed concentration,[c] mg/liter
Toxic organics					
1,1,1 trichloroethane	NA	NA	NA	NA	0.063
Methylene chloride	NA	NA	NA	NA	0.076
Toluene	NA	NA	NA	NA	0.113
Trichloroethylene	NA	NA	NA	NA	0.038
Total toxic organics	NA	NA	NA	NA	0.290
Toxic metals					
Antimony	0.126	0.188	0.153	0.153	0.111
Arsenic	0.100	0.160	0.121	0.119	0.080
Cadmium	0.135	0.217	0.172	0.171	3.218
Chromium	2.476	3.150	2.867	2.871	1.148
Copper	0.052	0.092	0.065	0.065	0.059
Lead	10.600	23.682	15.161	15.215	4.577
Nickel	0.070	0.121	0.093	0.093	0.076
Silver	0.001	0.002	0.001	0.001	0.004
Zinc	5.120	11.907	7.789	7.781	38.388
Non-toxic metals					
Aluminum	3.276	4.190	3.842	3.836	6.055
Manganese	0.040	0.061	0.051	0.051	0.019
Vanadium	0.003	0.010	0.006	0.006	0.005
Boron	7.080	9.520	8.580	8.637	12.841
Barium	0.586	1.759	0.990	0.993	0.484
Molybdenum	<0.035	0.098	0.054	0.053	0.050
Tin	<0.025	0.127	0.059	0.059	0.039
Yttrium	1.290	2.339	1.700	1.699	11.423
Cobalt	<0.050	<0.050	<0.050	<0.050	0.101
Iron	7.720	14.371	10.777	10.779	4.890
Titanium	<0.002	0.221	0.075	0.076	0.089
Other pollutants					
Cyanide, total	0.15	0.30	0.27	0.27	0.002
Oil and grease	11	14	12	12	62.3
Total organic carbon	43	58	49	50	134.6
Total suspended solids	50	130	89	90	143.1
Phenols	-	-	-	-	0.060
Fluoride	259	490	340	334	845.4

[a] Pollutant concentrations do not reflect dilute process wastewater discharged directly as well as process wastes unobtainable prior to wastewater treatment.

[b] Pollutant concentrations do reflect dilute process wastewater discharged.

[c] Single stream sample value developed from individual sampled raw wastes.

- = Detected at trace levels.

NA = Data not available.

Glass Panel Wash

1. Function - The steel aperture masks are inserted within a glass panel, with the result referred to as a panel-mask "mate". The mate is heat annealed and the components are separated. The glass panels are then washed in an acid bath and rinsed repeatedly with water. No additional operations are performed on the mask.

2. Input Materials - Hydrofluoric and sulfuric acids are used in this process.

3. Operating Conditions - The exact temperatures and pressures encountered during these process operations are not reported.

4. Utilities - Water is required for rinsing the glass panels. Specific quantities of water or other utility service required are not reported.

5. Waste Streams - There are no air emissions from this process.

Wastewater is produced during the glass panel wash, and there may be high concentrations of acids and fluorides. During the picture tube manufacturing process the panels are inspected at various points along the production sequence. A percentage of these panels are rejected and returned to the initial panel wash. Because of this quality control procedure, pollutants generated at the panel wash will include pollutants associated with the wastewater from process steps further down line on the production scheme, i.e., the photoresist and phosphor application steps. A characterization of wastewater from two television picture tube manufacturing plants is summarized in Table 8-3.[1]

There are no solid wastes from this process.

6. Control Technology - Wastewater from the panel wash at some plants is pH adjusted using sodium bicarbonate. The resulting neutral solution is allowed to settle. The wastewater discharged from this initial settling process flows through three additional settling tanks before it is discharged into the municipal treatment system.[1]

Photoresist Application[1,3]

1. Function - A chromium bearing photoresist solution is applied to the glass panel to prepare the surface for selective phosphor application. The photoresist solution is applied, the mask is placed over the panel, and the panel is exposed to light, developed, graphite coated, re-developed, and cleaned in several acid solutions. The photoresist application process results in a graphite-coated panel surface with a multitude of uncoated dots.[3] These dots will be the future sites of phosphor application.

2. Input Materials - The major input materials to this process include the photoresist solution containing chromium, the graphite coatings, developer solutions composed of hydrogen peroxide and deionized water, and hydrofluoric-sulfuric acid solutions.

3. Operating Conditions - The exact temperatures and pressures encountered during the photoresist process have not been documented.

4. Utilities - The types and quantities of utility service required for this process are not reported.

5. Waste Streams - There are no air emissions from this process.

Wastewater includes spent acid, photoresist, developer solutions, and rinses. It contains high concentrations of hexavalent chromium, strong acids, fluorides, graphite, and proprietary chemicals included in the photoresist solutions. A characterization of wastewater streams from several processes at two television picture tube manufacturing plants is summarized in Table 8-3.

The type or extent of solid waste generated during this process are unknown.

6. Control Technology - The photoresist and developer solutions require treatment to reduce the chromium before discharge to the environment. The chromium-bearing wastewater is reduced from the hexavalent to the trivalent state using sulfuric acid and sodium bisulfate. These partially treated wastes are subjected to further chemical treatment with sodium carbonate, calcium chloride, and sodium bisulfate. The chemically treated wastewater is then clarified and filtered before discharge to the environment. Figure 8-2 summarizes the waste treatment facility at one picture tube manufacturing process which handles hexavalent chromium wastes.[1]

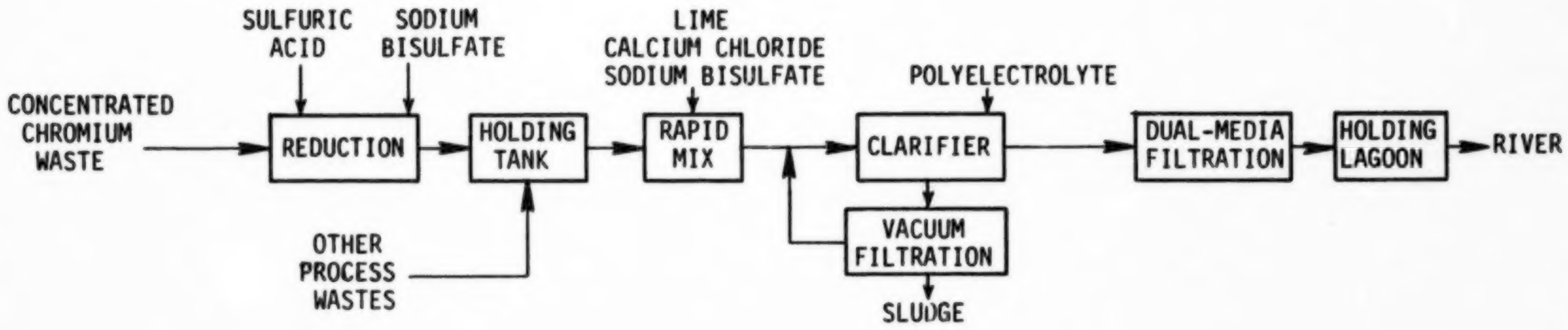
SULFURIC ACID
SODIUM BISULFATE
CONCENTRATED CHROMIUM WASTE
REDUCTION
HOLDING TANK
OTHER PROCESS WASTES
LIME
CALCIUM CHLORIDE
SODIUM BISULFATE
RAPID MIX
POLYELECTROLYTE
CLARIFIER
VACUUM FILTRATION
SLUDGE
DUAL-MEDIA FILTRATION
HOLDING LAGOON
RIVER

Figure 8-2. In-place waste treatment for hexavalent chromium wastes from a picture tube manufacturing process.

Phosphor Application

1. Function - The panels leaving the photoresist application process undergo another application of resists before deposition of phosphors. The phosphors are deposited onto the panel as three separate colors (red, blue, and green). The colors are applied to the glass panel as numerous triads of dots. The panel and mask are again mated, and the entire assembly is exposed to light. Next, the mask is removed and the panel is developed. A protective lacquer coating is applied to the panel in order to seal in the phosphors. Aluminum is vacuum-deposited onto the lacquered panel in order to enhance reflection. The mask is reunited with the panel and the mask-panel mate is cleaned first in an alkali, then in acid.

2. Input Materials - The main input materials to the phosphor application process include photoresist, phosphors, a protective lacquer coating, and aluminum. Photoresist or photosensitive solutions used in the picture tube industry commonly contain dichromates. The developer solutions used in connection with the photosensitive materials are composed of hydrogen peroxide and deionized water. The phosphors are the source of the color associated with modern television picture tubes. The red phosphors contain phosphor activated by the rare earth metals yttrium and europium. The blue phosphors contain zinc sulfide phosphors activated with silver. The green phosphors are zinc-cadmium sulfide phosphors activated with copper. The protective coatings used to cover the phosphor triads consist of either toluene-based lacquers or silicates.

3. Operating Conditions - The exact temperatures and pressures encountered during the phosphor application process are not documented in the literature.

4. Utilities - The types and quantities of utility service required for this process are not reported.

5. Waste Streams - There are no air emissions associated with this process.

Wastewater from the phosphor coating solutions, developer solutions, the aluminizing process, panel cleaning solutions, and associated rinses all contain high levels of phosphor. These contaminants include cadmium sulfide, zinc sulfide, yttrium, europium, and moderate levels of proprietary photoresists. A summary of the raw waste for two television picture tube manufacturing operations is given in Table 8-3.[1]

There are no solid wastes generated during this process.

6. Control Technology - Two categories of liquid waste streams are generated during the phosphor application process, phosphor waste and "other" pollutant wastes. These two categories are treated by different systems. The red, blue, and green phosphors are treated by individual systems, as shown in Figure 8-3. The composite waste stream containing non-phosphor-type substances is combined with other wastewaters and handled by the types of waste treatment schemes described in previous processes.

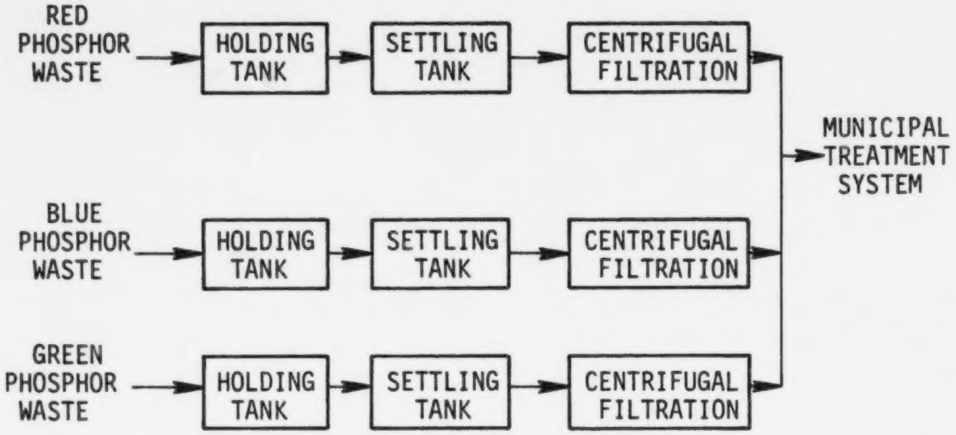
RED PHOSPHOR WASTE
HOLDING TANK
SETTLING TANK
CENTRIFUGAL FILTRATION
MUNICIPAL TREATMENT SYSTEM
BLUE PHOSPHOR WASTE
HOLDING TANK
SETTLING TANK
CENTRIFUGAL FILTRATION
GREEN PHOSPHOR WASTE
HOLDING TANK
SETTLING TANK
CENTRIFUGAL FILTRATION

Figure 8-3. In-place waste treatment for phosphor wastes from a picture tube manufacturing process.

Glass Funnel Preparation

1. Function - Glass funnels which are purchased from a supplier or produced offsite must be prepared before entering the picture assembly process. The glass funnels are first washed in an alkaline solution and then rinsed in water. The inner surface of the clean glass funnel is coated with graphite to prevent reflection within the picture tube. A lead glass frit is then applied to the glass funnel along the surface which will eventually be fused to the picture tube panel.

2. Input Materials - The glass funnel is made of specialty glass with enhanced structural and electrical characteristics. The graphite coating is free of additives or contaminants. The constituents of the lead frit and alkaline wash are not known.

3. Operating Conditions - The exact temperatures and pressures encountered during the glass funnel preparation process are not documented in the literature.

4. Utilities - The types and quantities of utility service required for this process are not reported.

5. Waste Streams - There are no air emissions from this process.

The wastewater discharge from this process contains a variety of heavy metals, including lead from the frit that was applied to the edge of the glass funnel. The wastewater also contains low levels of silicates. A summary of the raw waste from two television picture tube manufacturing operations is given in Table 8-3.[1]

There are no process solid wastes.

6. Control Technology - The treatment of wastewater discharge from this process was not specifically addressed in the literature. Lead-bearing wastes are concentrated and treated separately at one manufacturing operation; however, it is not clear whether the source of the lead waste was the glass funnel preparation process, another process, or the combination of all lead emitting processes. Treatment consists of chemical precipitation with sodium carbonate, with the effluent then transferred to holding tanks. The resulting lead carbonate material is land-filled.[1]

Shield Degreasing[1]

The electric shields are degreased before entering the final tube assembly. The nature of this degreasing operation, the input materials used, the operating conditions required for proper processing, and the existence of pollutant waste streams are not reported. Little information was available concerning this portion of the cathode ray television picture tube operation.

Electron Gun Assembly[1]

The electron gun mount contains the cathode and grid which provide electrons that bombard the light-emitting phosphor screen. The electron gun mount assembly process includes a cleaning operation prior to the final picture tube construction. The nature of this assembly process, the input material used, the operating conditions required for proper processing, and the existence of pollutant waste streams are not documented in the available literature.

Final Tube Assembly[1]

1. Function - The panel-mask mate with the finished phosphor coating receives a degreased electron shield. Following attachment of the shield, the assembly is heat-fused to the lead glass frit of the finished glass funnel. Next, the electron gun mount is heat-sealed to the base of the panel-funnel assembly. At this stage of construction, the assembly is described as a "bulb". The bulb is exhausted, sealed, and the cathode is aged by applying a current to the appropriate leads. The finished tube is tested, an external graphite coating is applied, and an implosion band is secured to the tube. The finished tube receives a final test before shipment.

2. Input Materials - Graphite is used in the exterior coating.

3. Operating Conditions - The exact temperatures and pressures encountered during the assembly of the picture tube are not reported.

4. Utilities - The types and quantities of utility service required for this process are unknown.

5. Waste Streams - The type and extent of air, water, and solid waste streams generated from this assembly process are not reported in the literature.

6. Control Technology - The type and extent of control technologies associated with this process are not known.

Picture Tube Reclaim[1]

1. Function - Some picture tube production facilities may have picture tube salvage and reclaim operations. The reclaim process includes the disassembly of spent picture tubes into panel, mask, and funnel components. The individual components are then reintroduced into the appropriate process operations within the production scheme.

2. Input Materials - The only item introduced into this process is the spent picture tube.

3. Operating Conditions - The exact conditions of operation developed for this process are not documented in the literature. It is assumed that the reclaim process is conducted at ambient temperatures and pressures.

4. Utilities - The types and quantities of utility service required for this process are not reported.

5. Waste Streams - There are no known air or liquid wastes from this process.

A variety of solid scrap materials (metal, glass, etc.) result from this process.

6. Control Technology - There is no documentation on the use of control equipment for this process.

REFERENCES FOR SECTION 8

1. U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and Standards for the Electrical and Electronic Components Point Source Category: Draft. EPA 440/1-80/075-a, October 1980.

2. Jacobs Engineering Group, Inc. April 1980. Draft Development Document for Effluent Limitations Guidelines, New Source Performance Standards for the Piezoelectric Crystals, Semiconducting Crystals, Phosphorescent Coatings and Magnetic Coatings Segments of the Electrical and Electronic Products Point Source Category.

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4. U.S. Department of Commerce. 1977 Census of Manufactures: Electrical Components and Accessories. June 1980.

5. Electronic Designs Gold Book, 1978/1980. Vol. 1 and 2. Hayden Publishing Co., Rochelle Park, New Jersey. 1979.

6. Electronic Industry Association Trade Directory and Membership List, 1979.

7. U.S. Environmental Protection Agency. Controlling Pollution from the Manufacturing and Coating of Metal Products: Water Pollution Control-II. EPA 625/3-77-009, May 1977.

APPENDIX

WASTEWATER TREATMENT AND CONTROL

The two best documented segments of the electronic component manufacturing industry are semiconductors and printed circuit boards. Wastewater effluents are the most significant environmental control problems associated with either of these production sequences. This appendix presents additional information on wastewater control strategies and technologies for these industries beyond that presented in the IPPEU format.

SEMICONDUCTORS

Control technologies employed for semiconductor device manufacture consist of both end-of-pipe and in-line systems.

End-of-pipe treatment systems employ segregation of waste streams into acidic wastes, fluoride wastes, and spent solvents. A typical treatment scheme is illustrated in Figure A-1; these technologies function as follows:

- Chemical precipitation (pH adjustment) - Dissolved heavy metal ions are often chemically precipitated as hydroxides using pH adjustment. This allows removal by physical means such as sedimentation, filtration, or centrifugation. Reagents commonly used to effect this precipitation include alkaline compounds such as lime and sodium hydroxide. Calcium hydroxide is used to precipitate phosphates as insoluble calcium phosphate. Solids formed in this step may be pumped to a sedimentation tank or allowed to settle in the precipitation tank. Hydroxide precipitation has proven to be an effective technique for removing many pollutants from industrial wastewater. It operates at ambient conditions and is well suited to automatic control.

- Sedimentation - Sedimentation is a process which removes solid particles from a liquid waste stream by gravitational force. Wastewater is fed into a high volume tank or lagoon where the suspended solids are allowed to settle. Because metal hydroxides tend to be colloidal in nature, coagulating agents or polyelectrolyte flocculants may be added to facilitate settling. Inorganic coagulants

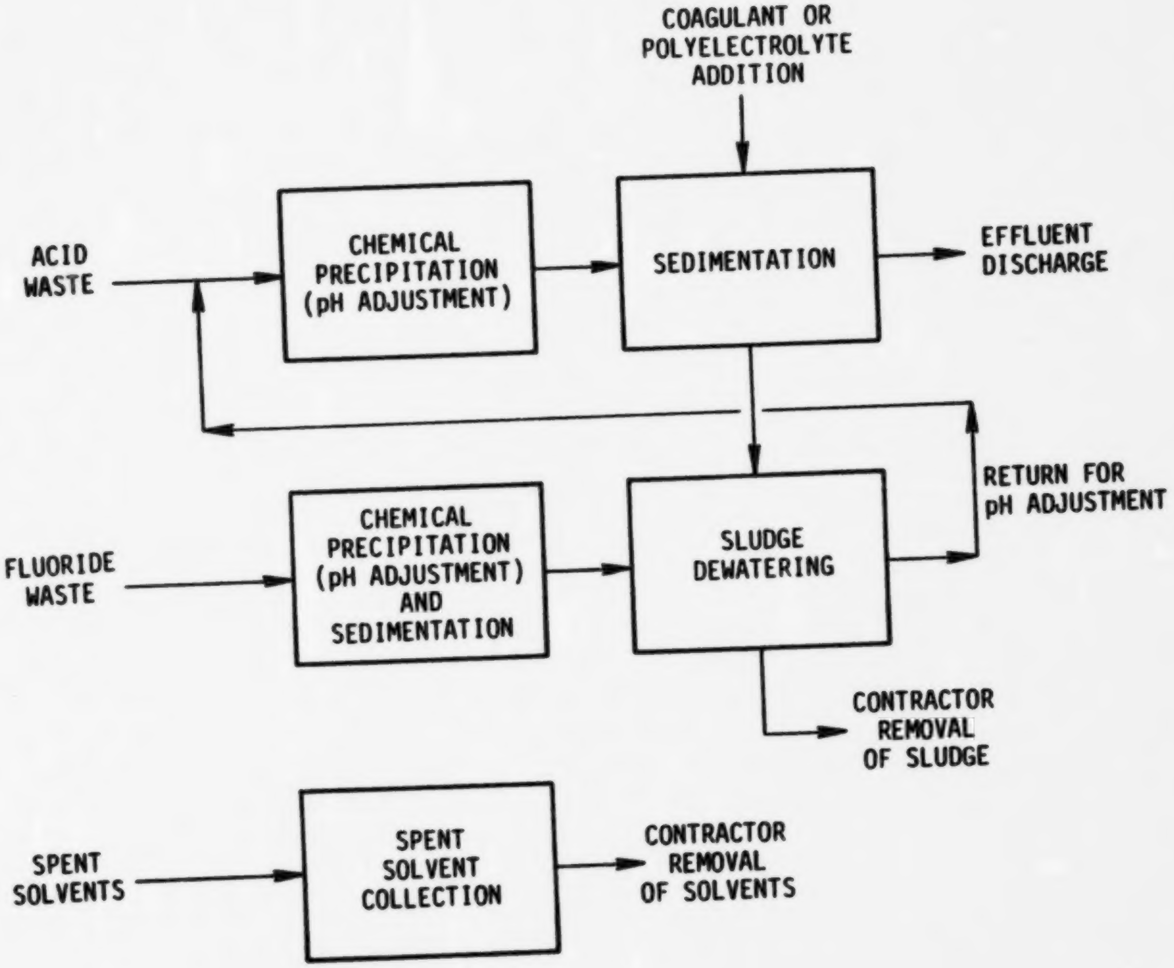
COAGULANT OR POLYELECTROLYTE ADDITION
ACID WASTE
CHEMICAL PRECIPITATION (pH ADJUSTMENT)
SEDIMENTATION
EFFLUENT DISCHARGE
RETURN FOR pH ADJUSTMENT
FLUORIDE WASTE
CHEMICAL PRECIPITATION (pH ADJUSTMENT) AND SEDIMENTATION
SLUDGE DEWATERING
CONTRACTOR REMOVAL OF SLUDGE
SPENT SOLVENTS
SPENT SOLVENT COLLECTION
CONTRACTOR REMOVAL OF SOLVENTS

Figure A-1. Wastewater treatment system - semiconductor manufacture.

include sodium sulfate, sodium aluminate, ferrous or ferric sulfate, and ferric chloride. Organic polyelectrolytes usually form larger floccules than coagulants used alone. Actual plant performance of chemical precipitation followed by sedimentation in the semiconductor industry in shown in Table A-1.[1] In general, sludges formed in this step are pumped to a sludge dewatering unit such as a vacuum filter, centrifuge, or filter press. The dewatered sludge is then contractor removed for off-site disposal.

- Fluoride treatment - Fluoride wastes are adjusted with lime to a pH of 11. This causes free fluoride ions to bond with calcium and settle out of solution. Sulfuric acid is then used to readjust the pH to 7.5, and polyelectrolytic flocculant is used to settle the solids more rapidly. The decanted water is discharged to the waste treatment system for further treatment prior to discharge, and the sludge is dewatered in a vacuum filtration unit and collected for contractor removal. Actual plant performance of fluoride treatment systems in the semiconductor industry is presented in Table A-2.[1]

- Solvent collection - Due to their high costs, segregation of spent organic solvents from wastewater is often economically attractive. Spent solvents can be contractor hauled to disposal sites, sent to recycling plants for regeneration and recovery, or recovered "in-house." In-house systems may incorporate activated carbon adsorption followed by distillation to purify the recovered solvent.

In-line treatment technologies rely upon reducing wastewater volume using water conservation techniques. This includes countercurrent rinsing, automatic shut-off equipment for rinse tanks, and rinse water recycle:

- Countercurrent rinsing - Semiconductor plants utilize two- to four-stage countercurrent rinses following process baths. Countercurrent rinses require much less water than a single overflowing rinse, yet provide equivalent removal of process chemical dragout from the wafer.

- Automatic shut-off equipment - The ultrapure water required by the semiconductor industry for process use must be in the range of 12 to 18 megohms of resistance. This measure of resistance reflects the presence of ions in the water. As the conductance of the water increases, the controller allows ultrapure water into the rinse until the desired resistivity level of the water is reached. At this point, the water flow stops until the conductivity controller senses another increase in the conductance. These conductivity controllers minimize the amount of make-up water added and provide high purity water for semiconductor wafer rinsing.

TABLE A-1. PERFORMANCE OF CHEMICAL PRECIPITATION AND SEDIMENTATION - SEMICONDUCTOR MANUFACTURE[1]

Parameter	Minimum concentration, mg/liter	Maximum concentration, mg/liter	Mean concentration, mg/liter
Arsenic	<0.003	0.005	0.004
Chromium	0.019	0.059	0.04
Copper	0.03	0.134	0.061
Lead	0.082	0.102	0.077
Nickel	0.520	0.844	0.541
Zinc	0.022	0.040	0.027
Oil and grease	2.4	17.4	6.46
Total suspended solids	<1.0	60.0	23.8
Fluoride	5.42	17.50	16.1
1,2,4-Trichlorobenzene	<0.01	<0.01	<0.01
1,1,1-Trichloroethane	<0.01	0.013	0.005
Chloroform	<0.01	0.02	0.013
2-Chlorophenol	<0.01	<0.01	<0.01
1,2-Dichlorobenzene	<0.01	<0.01	<0.01
1,3-Dichlorobenzene	<0.01	<0.01	<0.01
1,4-Dichlorobenzene	<0.01	<0.01	<0.01
Methylene chloride	<0.01	0.049	0.03
Naphthalene	<0.01	<0.01	<0.01
4-Nitrophenol	<0.01	<0.01	<0.01
Phenol	<0.01	<0.01	<0.01
Di-n-octyl phthalate	<0.01	<0.01	<0.01
Tetrachloroethylene	<0.01	<0.01	<0.01
Toluene	<0.01	<0.01	<0.01
Trichloroethylene	<0.01	<0.052	0.024

TABLE A-2. PERFORMANCE OF FLUORIDE TREATMENT SYSTEMS - SEMICONDUCTOR MANUFACTURE[1]

Parameter	Plant 1 mean concentration, mg/liter[a]		Plant 2 mean concentration, mg/liter[b]	
	In	Out	In	Out
Flow, l/hour	1049[c]	1049[c]	22,583	22,583
Arsenic	0.087	0.042	<0.01	<0.01
Cadmium	<0.003	<0.003	0.004	<0.001
Chromium	217.16	0.39	22.8	0.055
Copper	2.14	0.11	2.2	0.145
Lead	0.075	0.065	5.35	0.005
Mercury	0.0025	0.007	<0.001	<0.001
Nickel	0.145	0.2	0.69	0.065
Selenium	0.007	<0.005	<0.005	0.005
Silver	0.02	0.018	0.024	<0.01
Thallium	<0.03	<0.03	0.005	0.012
Zinc	0.11	0.218	<0.01	<0.01
Total suspended solids	4150	747.3	5.6	71.0
Fluoride	38750	24.3	760.0	37.0

[a] These values are means because these streams were sampled over three different sampling periods.

[b] These are single stream values.

[c] This is total flow in liter/h for three streams sampled.

Note: The "in" streams are not total raw waste streams and thus cannot be compared with values in summary of raw waste data, Table A-1.

- Rinse water recycle - Pollutants in the recycled process water are removed in the deionized water production area. As much as 50 to 80 percent of the total process water used may be recycled. When the components of deionized water production are backwashed and regenerated, the pollutants from reused rinse water and from supply water are sent to the waste treatment area for treatment prior to discharge. This reuse conserves water, concentrates the pollutants, and decreases wastewater discharge. All of these factors contribute to the cost effectiveness of end-of-pipe treatment processes.

PRINTED CIRCUIT BOARDS

Control technologies for printed circuit board manufacture also consist of both end-of-pipe and in-line systems.

End-of-pipe treatment systems for non-segregated wastes generally involve flocculation, clarification, and contract hauling of sludge. Chlorine is added to the flocculation tank for the oxidation of cyanides (if present). Lime is also added to the flocculation tank both to raise the pH for cyanide oxidation and to precipitate metals as hydroxides in the clarifier. End-of-pipe treatment systems employing segregation of waste streams generally separate wastes requiring treatment. Typical treatment methods are described below and shown in Figure A-2:

- Cyanide-bearing wastes - This stream is composed of rinses following any operation where cyanides are employed: cyanide copper plating, cyanide gold plating, and cyanide gold stripping. Treatment of these wastes involves oxidation of cyanides to cyanates and, in a second step, to nitrogen and carbon dioxide. Chlorine addition (in the form of sodium hypochlorite) is typically used to effect the oxidation while the pH is maintained (by sodium hydroxide or other base addition) at approximately 11. After oxidation, treated cyanide wastes may be combined with waste streams containing acid and alkali cleaners and other non-chelated metals.

- Acid-alkali and non-chelated metals streams - This stream consists of rinse waters following several operations: acid and alkali cleaners in all process lines, non-chromium and non-ammoniated etches, catalyst application, acceleration, and non-cyanide and non-chelated plating baths. This stream generally contains metals such as tin, palladium, lead, and copper. Treatment of these wastes involves flocculation using lime to precipitate metals followed by settling. This flocculation and settling can remove 95 to 98 percent of the metals, depending on the type of metals in the waste streams. Alternatively, membrane or diatomaceous earth filtration may be used to separate flocculated solids.

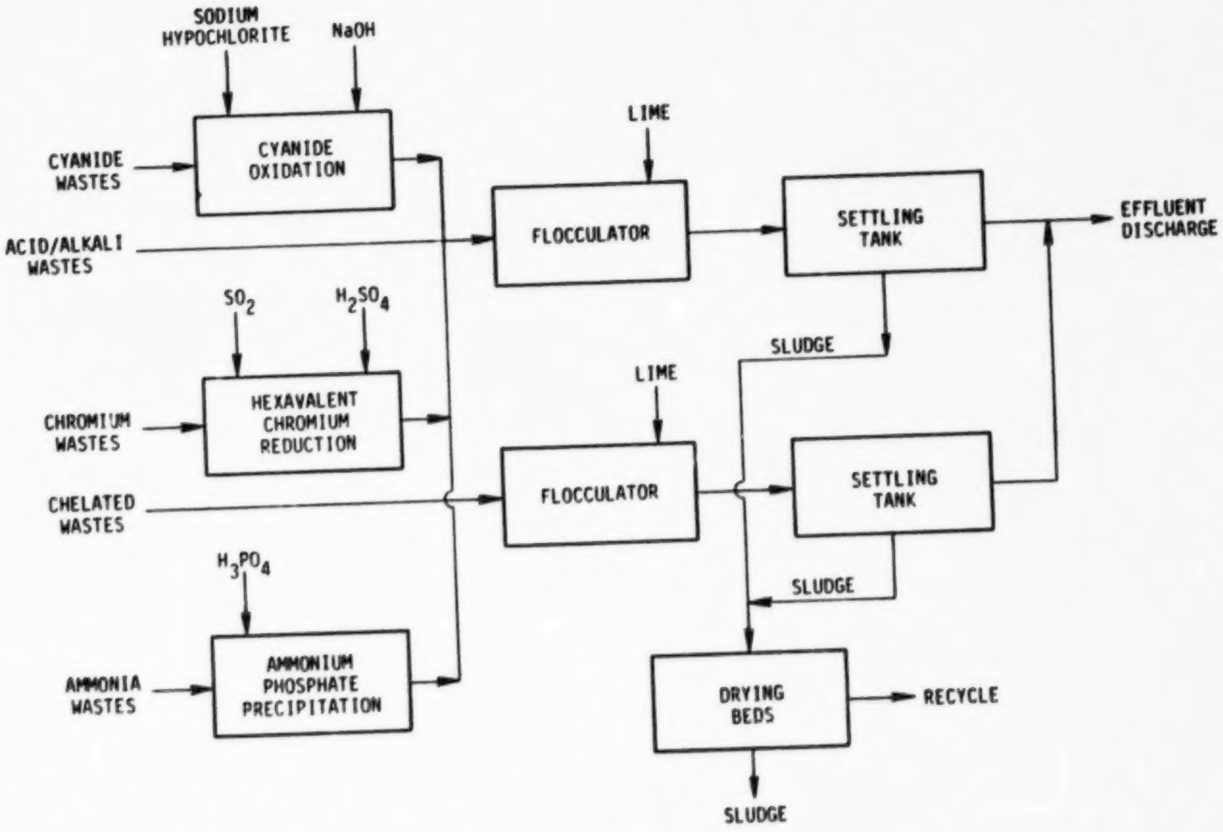
SODIUM HYPOCHLORITE
NaOH
CYANIDE WASTES
CYANIDE OXIDATION
ACID/ALKALI WASTES
SO_2
H_2SO_4
CHROMIUM WASTES
HEXAVALENT CHROMIUM REDUCTION
CHELATED WASTES
H_3PO_4
AMMONIA WASTES
AMMONIUM PHOSPHATE PRECIPITATION
LIME
FLOCCULATOR
LIME
FLOCCULATOR
SETTLING TANK
SETTLING TANK
SLUDGE
SLUDGE
EFFLUENT DISCHARGE
DRYING BEDS
RECYCLE
SLUDGE

Figure A-2. Wastewater treatment system - printed circuit board manufacture (segregated waste streams).

- Chelated waste streams - This stream consists of rinses following operations where chelating agents are present. Included in this group are electroless plating rinses. These wastes must be kept separate from other metal-bearing wastes. Treatment generally involves lime flocculation and settling or membrane filtration in a method similar to that described for acid-alkali and non-chelated waste streams.

- Chromium-bearing wastes - This stream contains hexavalent chromium from chromic acid etch rinses if such etching is used. This is usually not found in the printed board industry. However, if such a stream exists, the hexavalent chromium must first be reduced to the trivalent form by lowering the pH and adding sulfur dioxide or similar chemicals before introduction to the flocculation tank.

- Ammonia waste streams - These streams consist of ammonia-base etchants and rinses. Treatment involves pH adjustment (frequently using caustic) and live steam injection. The effect of these two steps is the precipitation of some metals and the dispersal of ammonia as a gas. Alternatively, phosphoric acid may be added to precipitate heavy metal ammonium phosphates. The treated ammonia wastes are then combined with the cyanide waste stream (following oxidation) and the acid-alkali and non-chelated waste streams.

In general, sludges formed in the flocculating and settling tanks are pumped to a sludge dewatering unit such as a vacuum filter, centrifuge, or filter press. The dewatered sludge is then disposed of at an on-site landfill or off-site by contract hauling.

In-line treatment technologies rely on wastewater volume reduction using water conservation techniques such as countercurrent rinsing, fog rinsing, and automatic shut-off equipment for rinse tanks. In addition, recovery of plating and etching solutions is practiced using techniques such as reverse osmosis, distillation, ion exchange, and electrochemical methods. Specific applications of in-line treatment techniques are discussed in Section 6.

REFERENCES

1. U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and Standards for the Electrical and Electronic Components Point Source Category: Draft. EPA 440/1-80-075a, October 1980.